Elucidation of Factors Influencing Molecular Weight and Thermal Stability of Poly(L-lactic acid) in Direct Polycondensation

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Contents

Chapter 1

General Introduction

1.1. Background of the work

In the 20th century, we have developed a society with material wealth by extending mass production and mass consumption type technologies, systems, and institutions. In the field of materials, various polymer materials such as polyethylene (PE) and polyethylene terephthalate (PET), etc. have been developed in addition to an ancient material such as wood and metal, and have played a part in improving the wealth of humankind. Polymer materials are indispensable materials for industrial use, and the global annual production exceeds 335 million tons. One cannot imagine life without polymer materials.

On the other hand, issues related to polymer materials cannot be ignored internationally. In the process of constructing mass production and mass consumption type society, as result of a large number of fossil resources have been consumed, the global environmental crisis is caused by plastic waste, global warming accommodating with carbon dioxide (CO_2) emissions in the incineration of plastics. Recently, microplastic pollution in the marine environment is being closed up as a global issue.

These problems are exerting a serious impact on life on Earth including humankind. What society should make is to encourage the world change from the mass production and mass consumption type system to a sound material-cycle society and high resource productivity society in order to toward everyone constructs sustainable development society.

A bio-based polymer using biomass, which is a renewable non-fossil resource as a carbon source, attracts attention as one solution. The bio-based polymer, which can contribute to reducing CO_2 emissions from the viewpoint of carbon neutral, is a material that plays an important role in establishing a sustainable development society and is expected as a material that can contribute to measures against global warming. In order to promote and develop bio-based polymers for society, it is significant to advance research related to the manufacturing, physical properties, and processing of bio-based polymers.

1.2. Bio-based Polymers

Bio-based polymers are manufactured by chemical or biochemical synthesis based on renewable bio-based raw materials. It has also been proposed to call plastic materials obtained from biomass related to bio-based polymers as biomass plastics. JBPA (Japan BioPlastics Association) and EUBP (European bioplastics) classify materials named as Bioplastics into two main categories [1]. They comprise of a whole family of materials with different properties and applications. According to the association, a plastic material is defined as a bioplastic if it is either bio-based, biodegradable, or features both properties. Biodegradable polymers are defined as plastics with similar properties to conventional plastics, but having biodegradation that is a chemical process during which microorganisms that are available in the environment convert materials into natural substances such as water, carbon dioxide, and compost. The Bioplastics may be classified into three main categories based on their origin and property (Table 1.1): (1) non-biodegradable polymers such as bio-based PE and polypropylene (PP), or partially bio-based bio-PET, (2) biodegradable polymers based on fossil resources such as poly(caprolactone) and poly(glycolic acid) ,

Table 1.1 Classification of bioplastics

	Fossil fuel	Fossil fuel + Bio-based	Bio-based
Biodegradable	Poly(vinyl alcohol) Poly(glycolic acid) Poly(caprolactone)	Baio-based Polybutylene succinate Poly(Lactic acid)/Polybutylene adipate terephthalate blend Starchp /Polyester blend	Poly(Lactic acid) Poly(hydroxyalkanoate)
Non-biodegradable	Polyethylene Polypropylene Polyethylene terephthalate Polystyrene Polyvinyl chloride Acrylonitrile butadiene styrene Polycarbonate Polyamide 6 etc.	Bio-based Poly(ethylene terephthalate) Bio-based Poly(trimethylene terephthalate) Bio-based Polyamide Bio-based Poly(carbonate)	Bio-Poly(ethylene) Polyamide 11

(3) biodegradable polymers based on bio-based such as poly(lactic acid) (PLA) and polyhydroxy alcohol (PHA). The combined production capacity of biodegradable polymers and biobased polymers in the world exceeds 2 million tons annually. Fig. 1.1 shows global production capacities of bioplastics 2018 by material type [1].

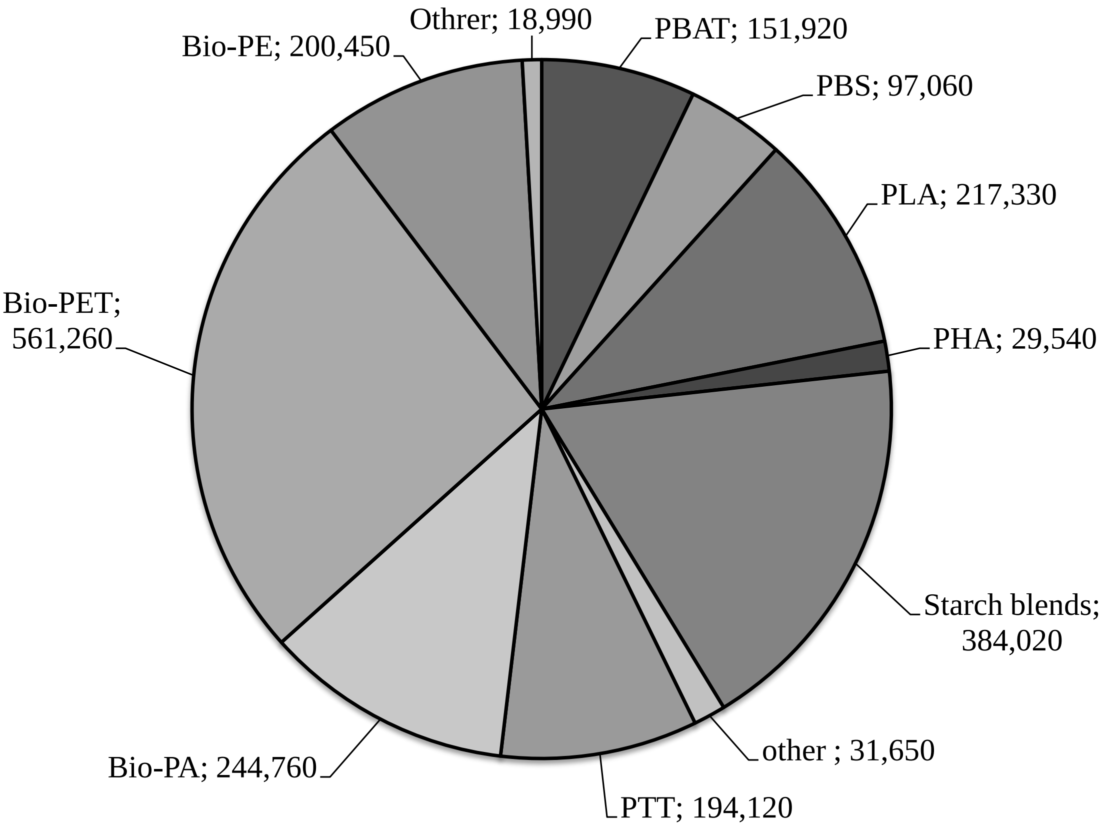

Fig. 1.1. Global production capacities of bioplastics 2018 by material type. The numerical unit is ton.

In Japan, it is shipped nearly 40,000 tons annually, about 0.4% of the total amount of plastic used. Meanwhile, as a national effort, the Ministry of the Environment is advancing policies for the spread of biomass plastic. In the 4th Fundamental Plan for Establishing a Sound Material-cycle Society, the target of domestic shipment of biomass plastics is 1.97 million tons by 2030 (Table 1.2), aiming for bioplastic substitution from petroleum-derived plastics [2].

Table 1.2 Indicators and numerical targets on biomass plastics in Japan by 2030

Item		Indicators	Annual goal	Numerical target (kt)	Estimated CO_2 emission reduction (kt-CO_2)
Integrated approach with sustainable society	Integrated improvement of circulation and low carbon	Biomass Plastics Domestic Shipment Volume	2030	1970	2090

In addition, research and development on bio-based polymer are advancing the following direction.

(1) Bio-based conversion of petroleum synthetic plastics: Biopolyethylene manufactured from glucose via bioethanol has already been supplied in full scale by

Blaskem Ltd. and is being used for shampoo refill containers and shopping bags. Bio-PET utilizing bio-derived ethylene glycol has also begun to be used in beverage makers. Since these bio-based plastics have exactly the same structure as petroleum synthetic plastics, existing bio-based plastics are expected to further expand in the future as it is possible to use existing molding processing equipment and technology as they are.

(2) Creation of new bio-based polymers: The United States Department of Energy has proposed 12 core substances derived from sugars as bio-based monomers [3]. Although these mass production processes have not been established, studies on using these 12 kinds of core materials as materials are underway. Miller et al. have reported a synthesis of polylactam from itaconic acid, with high glass transition temperature and with hydrolyzability faster than PLA [4]. It is expected that many new bio-based plastics using glycerin, sorbitol, etc. will be developed in the future.

(3) Increase productivity and improve the performance of existing bio-based polymers: PLA has been extensively researched and developed in this field as biodegradable plastic or bio-based plastic. As a result, research on PLLA has progressed

from basic research to applied research, and practical application has advanced considerably. On the other hand, a lot of tasks have also been clarified towards popularization, and problems to be studied still remain.

Since lactic acid has a chiral methine carbon, two different structural forms exist in its polymer, i.e., poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA). In addition, poly(D,L-lactic acid) (PDLLA) having different D, L ratios of lactic acid units, stereocomplex polylactic acid (sc-PLA) obtained by mixing PLLA and PDLA, and stereoblock type polylactic acid (sb-PLA) in which D and L chains of lactic acid are arranged in a block, all of which have different properties. In general, homopolymer properties such as thermal properties, mechanical properties and crystallization behavior are affected by their molecular weight and optical purity (*OP*). PLA has high transparency and rigidity, and the crystalline polymer PLLA has a melting point of 170 to 180 °C which is close to the melting point of general purpose polypropylene. The crystal melting temperature of sc-PLA is 230–240 °C [5], which is 50 °C higher than the melting point of a homopolymer of PLLA or PDLA and has been studied for applications requiring heat resistance. In order to enhance hydrolysis resistance, impact resistance and processability, studies of polymer structure control, polymer blend, polymer alloy etc. have been also being conducted. The amount of PLA supplied worldwide is over 200,000 tons per year, and it is used in a wide range of fields including packaging containers, housings, and automobile parts, and expansion of use is expected in the future.

1.3. Production of Poly(L-lactic acid)

PLLA can be prepared by two different polymerization process from lactic acid: one is ring-opening polymerization (ROP) of L-lactide and other is direct polycondensation of L-lactic acid.

ROP is the most commonly route to obtain high molecular weight of PLLA. The ROP process consists of multi steps from L-lactic acid monomer. The L-lactide, which is a cyclic lactic acid dimer, is formed in the first step by depolymerized of PLLA oligomer through an internal transesterification, i.e., by back-biting reaction to L-lactide. The molecular weight and melting point of PLLA obtained by ROP are influenced by the purity of the L-lactide monomer, the obtained L-lactide undergoes a purification process. The purified L-lactide is converted into the high-molecular weight PLLA by catalytic ring-opening polymerization. Ring-opening polymerization was carried out most commonly by a stannous octoate catalyst. It is also reported that alkylmetals and metal halides, oxides, carboxylates and alkoxides are very effective in the synthesis of PLA on ROP. Gupta et al review a study of more than 100 catalysts for the synthesis of PLA [6]. Alcohol is used as an initiator, and the molecular weight is generally adjusted by the addition amount thereof on the ROP using Sn catalyst. ROP process is industrialized, PLLA can be produced at low cost from L-lactic acid. The commercial PLLA, for examples, Nature Works LCC (USA) and Corbion Co. Ltd (Netherlands) is manufactured by this ROP process. The center of the manufacturing technology is how to purify L-lactide, and the purification technology of L-lactide is a factor affecting the price of PLLA.

Since L-lactic acid monomer existence of both a hydroxyl and a carboxyl group, it can be converted directly into polyester through a polycondensation reaction. If PLLA can be directly synthesized from lactic acid in one step, the polymerization process becomes simpler and leads to make PLLA low cost. However, it was believed that a PLLA with high molecular weight could not be prepared by the direct polycondensation of L-lactic acid because of the difficulty in driving the dehydrative equilibrium to the direction of esterification and it is hard to remove water completely from the highly viscous reaction mixture.

The solution polycondensation developed by Ajioka et al. brought a breakthrough in increasing the molecular weight of the polycondensation of L-lactic acid [7,8]. This polymerisation technique allows a reaction temperature to be chosen below the melting point of polymer, and thus efficiently prevents depolymerisation and racemisation during polymerisation. It has been reported that PLLA with high molecular weight can be produced by this method. PLLA obtained by this solution polycondensation have shown that the glass transition temperatures same as PLLA synthesized by the ROP process of lactide, but that has a lower melting point than lactide process. The mechanical properties of the two polymers were also very similar. However, the using of solvents such as diphenyl ether results in the complexity of the process control, leaving the price of PLLA expensive. Also, it is hard to remove the solvent completely from the end product.

Also, Moon et al. have succeeded synthesis of PLLA by another direct polycondensation method. They obtained a high-molecular-weight PLLA (> 10^5 Da) by founding a new synthetic procedure of PLLA combing melt polycondensation (MP) and solid-state polycondensation (SSP) [9–11].

MP of L-lactid acid is carried out in three stages: removal of the free water, oligomer polycondensation and melt condensation of high molecular weight PLLA. In first and third stages, the removal of water is the rate determining step. For the second one, the rate determining step is the chemical reaction, which depends on the catalyst used. MP generally produces PLLA oligomers with average molecular weights from several thousand to several ten thousand and other side reactions also can occur, such transesterification, resulting in the formation of ring structures as lactide. That subproducts production cannot be excluded but can be controlled by the use of appropriate catalysts and functionalization agents, such as $SnCl_2$/p-TSA system, as well as by varying the polymerization conditions.

In the SSP, the melt-polycondensated PLLA is cooled below its melting temperature, followed by particle formation, which then subjected to a crystallization process to prevent agglomeration of particles. A semicrystalline solid prepolymer, of relatively low molecular weight, in powder or pellet form, is heated to a temperature below T_m but above T_g in the presence of a suitable catalyst. The polymer terminals can be concentrated in the amorphous region and connected with each other effectively by esterification. The polymer chains thus elongated can participate in crystallization around the crystal-amorphous borders. A high-molecular-weight PLLA (> 10^5 Da) is obtained after 20 h on SSP [11]. Although, SSP takes a considerably longer time, very high molecular weight PLLA can be obtained, which cannot be accomplished in melt or solution polymerization, owing to viscosity restrictions and hydrolytic, thermal and oxidative degradation. Almost all catalysts for MP can be subjected to as catalysts for SSP.

In summary, this direct polycondensation processes is expected to relatively economical and easy to control, but they are equilibrium reactions affected by numerous parameters such as the temperature, the reaction time, catalysts, pressure, and so on.

1.4. Crystallization of Poly(L-lactic acid)

Different crystal structures have been reported for PLLA, the formation of which depends on the crystallization conditions. The most common α-form, which is left-handed 10_3 helices in the pseudo-orthorhombic crystal lattice, occurring in conventional melt and solution crystallization conditions were first reported by De Santis et al. in 1968 and investigated further in a number of study [12,13]. The unit cell accommodating two PLLA chains has dimensions of 1.07, 0.645, 2.98 nm in a-, b-, and c-axis, respectively. Kobayashi et al. reported different dimensions of 1.05, 0.61, 2.88 nm in a-, b-, and c-axis, respectively.

Zhang et al reported another disordered α-form crystal which is named α’-form for PLLA crystallized below 120 °C [14]. In the wide angle X-ray diffraction (WAXD), the chain conformation and crystal system of the α’-form is similar to α structure, but with a looser and less ordered chain packing. Some minor diffractions attributed to (004/103), (204), (015), and (016) are absent in WAXD measurement of the α crystal [15]. Further investigation suggests that only the α crystal is formed at crystallization temperatures below 100 °C while crystallization between 100 and 120 °C gives rise to the coexistence of α’ and α crystal structures [16]. The thermal data of α-form crystal have been widely investigated. Fischer et al. reported determined the heat of fusion (ΔH_m) for the ideal α-form crystals as 93.1 J/g according to Flory’s equation [17].

Numerous studies have been done on the parameters affecting melting behavior of PLLA. The T_m of PLLA is affected by optical purity, which is D-lactic acid unit content in the polymer, molecular weight, and crystallization conditions. Saeidlou et al. compares the T_m of PLLA data from several authors as a function of D-lactic acid unit content in the polymer [18]. They reported that pure PLLA which did not include D-lactic acid unit exhibits the maximum melting temperature, between 175 and 180 °C depending on authors. The T_m decreases linearly with the D-lactic acid unit content. Molecular weight is also another factor that significantly influences the melting temperature. The T_m of PLLA increases dramatically with molecular weight for low number averaged molecular weight ($\mathrm{M_n}$) but reaches an asymptotical value at $\mathrm{M_n} > 100$ kg/mol, when compared between the T_m and the $\mathrm{M_n}$ on the PLLA with same D-lactic acid unit content. Crystallization temperature and time also affect melting behavior of

PLLA [19]. Due to different crystallization temperature and processing time, the melting peak shows a unimodal or bimodal peak.

Also, crystallization behavior of PLLA is depended on molecular weight, optical purity, and annealing condition. Several studies focused on molecular weight dependences of crystallization and melting behavior of PLLA [20,21]. They revealed that the crystallization rate of PLLA drops dramatically as the molecular weight increase due to the higher restrictions of chain motion. PLLA having lower molecular weight showed a tendency to form α-form. Laura et al. investigated that effect of optical purity of PLLA on the crystal polymorphism [22]. They revealed that pure PLLA (0% D-lactic acid unit content) displays a high crystallization rate. While, the presence of D-lactic acid, introduced in the PLA chain induces not only a decrease of the crystallization rate of PLLA but also affects the temperature range where α and α’ modifications grow. Saeidlou et al. plotted the crystallization growth rate vs. crystallization temperature for PLLA of similar molecular weight but with different D-lactic acid unit content [18]. This plot displays that increasing the optical impurity decreases dramatically the maximum spherulite growth rate. The spherulite growth rate of PLLA decreases by a factor of 40 by including only 6.6 % of impurity of the D-lactic acid unit.

The relation between the numbers of crystallization sites (spherulite density) with crystallization temperature for PLA is also investigated. The spherulite density was shown to decrease with temperature and the decreasing rate gradually accelerates with temperature [18,23,24]. The fastest crystallization rates are observed in the 100–130 °C temperature range.

Studies on the crystallization behavior of PLLA as described above are based on polymers that have been made to some extent high molecular weight. In the application of direct polycondensation of polylactic acid, it is also necessary to elucidate the crystallization behavior during the SSP.

1.5. Purpose of this Study

Numerous studies have been conducted from the first synthesis of PLLA by Carozas to the present, such as polymerization of PLLA, crystal structure, mechanical properties, processing, application and so forth. As a result, PLLA has become one of the bio-based polymers that have been produced industrially, and it is now being used on the scale of over 200,000 tons a year worldwide [1]. It is expected that utilize of PLLA will continue to expand towards the development of a sustainable society.

On the other hand, the industrial production method of PLLA has been still manufactured by the L-lactide method having multi-step processes. The direct polycondensation of L-lactic acid combining MP/SSP, which is expected to be superior in terms of energy and cost, has not been applied industrially because optimization of process conditions and factors influencing polymerization and so forth have not been clarified. A significant increase in molecular weight of PLLA in direct polycondensation occurs during SSP and is an important part of this process. It has been reported that the crystallization state in SSP affects the molecular weight of the resultant PLLA in a few of studies, however, the crystallization behavior during SSP, as well as the relationship between molecular weight and crystallization have not been still clarified [10,25]. In applying direct polycondensation to industrialization, it is necessary to elucidate the polymerization behavior in SSP. Polycondensation of lactic acid is actually an esterification reaction of the carboxyl and hydroxyl groups. A number of catalysts for direct polycondensation have been studied to efficiently progress the esterification reaction while suppressing side reactions. In addition, since the residual catalyst affects the physical properties of the resultant PLLA and applicable applications, catalyst design taking account of the influence after polymerization is also significant. In the reports so far, the amount of catalyst in direct polycondensation is more than 10 times greater than the lactide method, so it is particularly necessary to consider residual catalyst in future applications. The Sn(II) compound has been utilized as the most popular catalyst in the MP/SSP of PLLA. However, the Sn(II) compound, showing toxicity, is hardly removed from the polymeric product, and the resultant PLLA containing the remaining Sn(II) may have limited use as materials. Furthermore, it has been reported that the remaining catalyst is likely to deteriorate the thermal stability of the polymeric products.

In the first study, relationship between the increase in molecular weight and evolution of crystal structure was studied in SSP of PLLA. DSC, Wide- and small-angle X-ray scatterings were measured to reveal crystal structure of PLLA in the SSP. The crystal morphology of the annealed samples was found to strongly influence the final molecular weight of PLLA in the SSP.

In the second study, several aromatic sulfonic acids having different number of alkyl substituents were examined as the organic catalysts of MP/SSP. Their degradation temperature of sulfonic acids was found to give strong influence on the degree of polymerization and thermal stability of the PLLA finally obtained. It was reported that how the sulfonic acids can work as catalysts in the SSP and how they can be removed from the SSP products by their thermal annealing.

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Chapter 2

Molecular Weight Increase Driven by Evolution of Crystal Structure in the Process of Solid-State Polycondensation of Poly(L-lactic acid)

2.1. Introduction

Poly(L-lactic acid) (PLLA) is a well-known biodegradable and bio-based polymer, which has been utilized in many applications such as disposable commodities, packaging films, and non-woven fibers because of its reasonable cost-property balance. There are two synthetic routes to PLLA: ring-opening polymerization (ROP) of L-lactide and direct polycondensation of L-lactic acid. Although the latter process is a one-step reaction, the former ROP process needs an extra process of synthesis of L-lactide monomer, which involves both depolymerization of PLLA oligomers and purification of the obtained L-lactide prior to the polymerization [1–6]. In spite of the multi-step process, ROP has been adopted for industrial production of PLLA because it is easier in controlling the polymerization process. Since the direct polycondensation method still remains in a pre-matured state, the process control has not yet been well established, making it difficult to compete with the ROP method.

Chapter 2

Various attempts have been made in the past two decades to develop an efficient method of direct polycondensation for obtaining PLLA polymers with high molecular weight because of its potential in cost reduction by large scale manufacturing [7–20]. Previously, Moon et al. developed a new synthetic procedure of PLLA by combing melt-polycondensation (MP) and solid-state post-polycondensation (SSP) [10–12]. They succeeded in obtaining a high-molecular-weight PLLA ($> 10^5$ Da) after the SSP. They expanded this method to the synthesis of stereoblock copolymers consisting of PLLA and poly(D-lactic acid) (PDLA) [21–24]. These processes may have similarity with the SSP of other condensation polymers such as poly(ethylene terephthalate) (PET) for which many researchers focused on the effects of the initial molecular weight and pre-crystallization of the precursory polymers, byproduct diffusivity, catalyst concentration, and crystallinity change on the molecular weight of the final polymers as well as on the kinetics of the SSP [18,19,25–28]. It was shown that the reaction rate of SSP depends not only on the diffusion of end groups in amorphous domain but also on the diffusivity of byproducts (condensed water) from the interior to exterior of solid polymer particles, which should be closely related with by the crystal structure of the reactant solid polymers. Thus far, the general crystallization behavior of PLLA has been extensively studied in terms of crystallization rate, crystal size, growing geometry, and lamellar organization [29–40]. These studies have been based on PLLA samples having high molecular weights, and in which the heat-treatment time for crystallization has not been so long as the reaction time needed for SSP. In addition, less attention has been paid to the relation between the crystal structure change and the molecular weight increase, although it should be a key factor for obtaining a high-molecular-weight PLLA in high yield by the successful SSP [18,19].

Moon et al. first reported the importance of crystallinity of PLLA in increasing the molecular weight [11]. Later, Peng et al. reported that the crystallinity determined in the stage of annealing of PLLA prepolymers significantly influences the increase in molecular weight of the PLLA polymers produced by the following SSP [18]. However, further study is needed to clarify the relationship between the evolution of crystal structure and molecular weight increase during the SSP of PLLA, especially for obtaining a PLLA having high optical purity for which crystal morphology and polymerizability ought to be different from those reported before. In consequence, it will be possible to optimize the SSP process and open a novel efficient route to the synthesis of PLLA with high molecular weight and optical purity, and by which the current ROP method can be replaced.

In Chapter 2, PLLA prepolymer by MP was first prepared and subjected it to SSP to investigate the relationship between the crystallization behavior and molecular weight increase of the PLLA polymers. Here, the changes in crystallinity, long period, and lamellar thickness were analyzed during the SSP by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), and small-angle X-ray scattering (SAXS), respectively, to observe their influence on the changes in molecular weight that were monitored by gel permeation chromatography (GPC).

2.2. Materials and Methods

2.2.1. Materials

L-Lactic acid (LA, HiPure 90) containing 10 wt% of water was commercially supplied by Corbion Purac (Gorinchem, Holland). Dodecylbenzenesulfonic acid

(DBSA) was purchased from Tokyo Chemical Industries, Co. Ltd. (Tokyo, Japan). All these materials were used without purification.

2.2.2. Melt Polycondensation

Melt polycondensation (MP) was conducted to obtain a PLLA prepolymer as follows. L-Lactic acid and DBSA (0.7 wt% amount relative to L-lactic acid) as a catalyst were charged into a flask and mixed under mechanical stirring. The mixture was then heated at 150 °C under 30 mmHg for 3 h. The generated water was trapped in a cold vessel connected to a vacuum pump throughout the MP. A PLLA prepolymer having a molecular weight of several thousands and melting temperature (T_m) around 140–155 °C was finally obtained. It was quenched in a cold bath for keeping amorphous state.

2.2.3. Solid-state Polycondensation

The PLLA prepolymer obtained above was pulverized with an electrical mill (WB-1, Osaka Chemical Co., Japan) to a size less than 150 μm in diameter, and the resulting powders were divided into several test tubes. Each tube was annealed by increasing the temperature from 80–110 °C for 2.5 h to make the powdery prepolymer crystallize and then heated at a predetermined temperature under 10 mmHg for a predetermined time to conduct SSP. The finally obtained product was then analyzed.

2.3. Measurements

2.3.1. Analytical Methods of General Properties

Number- (M_n) and weight-average (M_w) molecular weights and dispersity (M_w/M_n) of PLLA polymers were determined by GPC on an apparatus with a refractive index detector (GL-7454, GL Science Inc., Japan). A combination of three columns (Shim-pack GPC-802C, 804C and 806C, Shimadzu Co., Japan) were used at 40 °C with chloroform as the mobile phase. Polystyrene (PS) standards were used to calibrate the relative molecular weights. The optical purity (*OP* in %ee) of the PLLA products was determined by the following formula:

$$OP\ (\%\mathrm{ee}) = 100 \times (L - D) / (L + D)$$

Where L and D denote the contents of L- and D-lactate units, respectively. To determine L and D, a portion of a polymer sample was hydrolyzed in a 2 *N* NaOH for 12 h at room temperature, and the resultant solution was neutralized with 1 *N* H_2SO_4. Then, the contents of L- and D-lactic acids were determined by high-performance liquid chromatography (HPLC) on a system with a UV detector (LC-20A, Shimadzu) at 254 nm. A resolving column (MCI gel CRS10W, Mitsubishi Chemical Co., Japan) was used at 35 °C with 1 mM $CuSO_4$ as the mobile phase.

2.3.2. Analytical Methods of Crystal Structure

The melting temperature (T_m), crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) of polymer samples were determined by DSC on a DSC-50 thermal analyzer (Shimadzu) at a heating rate of 10 °C/min. The crystallinity (X_c) was calculated by the following equation:

$$Xc = (\Delta H_m - \Delta H_c) / \Delta H^0{}_m$$

where $\Delta H^0{}_m$ is the specific heat of fusion of PLLA crystal, i.e., 93 J/g.

WAXD measurements were conducted on a refractometer (CN4037A1, Rigaku Co., Japan) with a Cu-Kα radiation (wavelength $\lambda = 0.1542$nm). SAXS measurements were performed using a refractometer (Nano-Viewer, Rigaku) with Cu-Kα radiation. Three collimation pinholes (0.8, 0.7, and 0.8 mm for the first, second, and third slits, respectively) were utilized for adjusting the beam size. The two-dimensional SAXS images were recorded by using a two-dimensional detector (PILATUS 100K, DECTRIS Ltd., Switzerland) to obtain the intensity data (I) as a function of 2θ scattering angle. The sample-to-detector distance was 590 mm, covering an angular range of $0 \leq q \leq 1.0$ Å ($q = (4\pi/\lambda)\sin(\theta/2)$, where q, λ and θ are scattering vector, X-ray wavelength, and scattering angle, respectively. The SAXS profile recorded was corrected by the Lorentz factor q^2 prior to obtaining the one-dimensional correlation function, $\gamma(r)$. The background intensity was subtracted from the scattering intensity. The function $\gamma(r)$ was calculated from the corrected SAXS profile using the following equation in reference previously reported by Xia et al [41].

$$\gamma(r) = \frac{\int_0^\infty q^2\, I(q) \cos(qr)\, dq}{\int_0^\infty q^2\, I\,(q) dq}$$

where $I(q)$ is the scattering intensity after the Lorentz correction and the denominator in the above equation is the total integrated intensity or invariant Q. The $\gamma(r)$ can be used to determine the values of long period (L), crystalline lamellar thickness (l_c), and amorphous layer thickness (l_a). The L is the summation of both l_c and l_a that is $L = l_c + l_a$ by neglecting the interfacial thickness. The average L was obtained by finding the peak position of the first maximum in γ(r). The self-correlation triangle method was used to determine the value of thickness l_2 and l_1(= L – l_2), which is estimated by the interception of the linear extrapolation in the initial portion of γ(r) curve with a horizontal line tangent to the first minimum peak of γ(r) curve. Fig. 2.1 illustrates a typical plot of γ(r) in the case of real lamellar stacks of crystalline and amorphous layers with which L, l_1, l_2 and Q were determined.

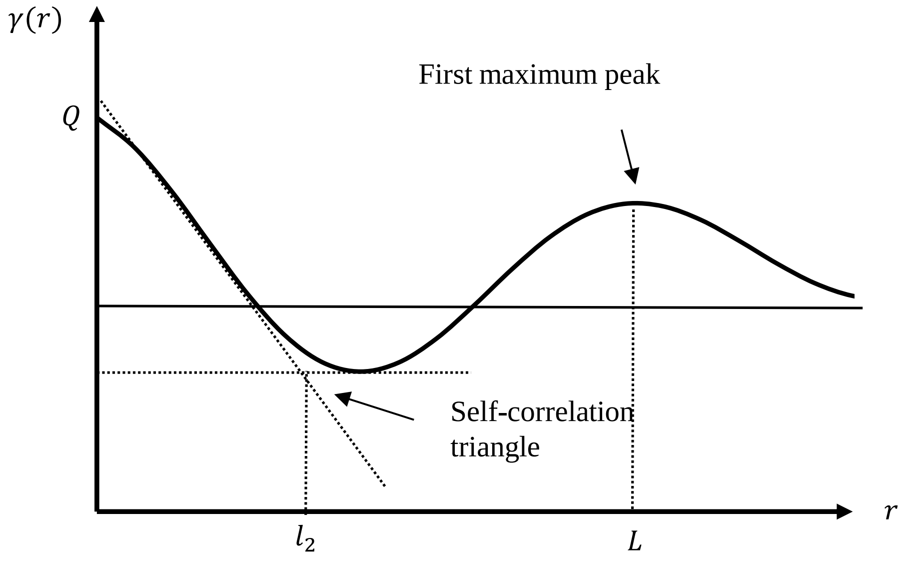

Fig. 2.1. A typical plot of a one-dimensional correlation function γ(r) for a real lamellar structure.

The value of either l_1 or l_2 can be assigned to the crystal thickness (l_c) since the correlation function method cannot distinguish which thickness value represents the crystalline phase. This point is discussed in the later section. The linear crystallinity wc was calculated by the following equation:

$$wc = (l_c / L)$$

2.4. Results and Discussion

2.4.1. Preparation of a Poly(L-lactic acid) Prepolymer

Organic sulfonic acids have been known to be effective catalysts in the solution polycondensation of L-lactic acid to produce PLLA having medium molecular weights [8–9]. Several aromatic sulfonic acids as the catalysts in the bulk MP of L-lactic acid were re-examined. Among benzene-, toluene-, and p-xylene sulfonic acids and DBSA, the best control in terms of catalytic activity was given by DBSA whose decomposition temperature was the highest, exceeding 200 °C. DBSA was found to keep its activity throughout the SSP taking long reaction time, while the other sulfonic acids were likely to decompose around 150 °C and lose its original activity (Fig. 2.2). Therefore it was decided to use the robust DBSA as the catalyst in this chapter.

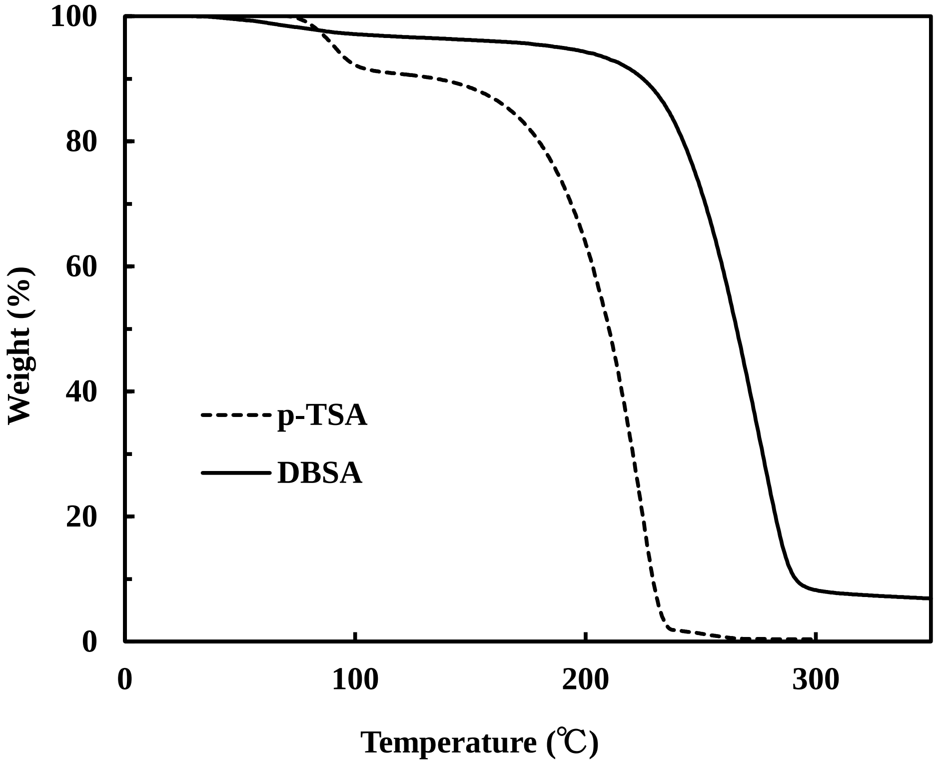

Fig. 2.2. Thermal decomposition temperature of p-TSA and DBSA

To obtain a PLLA prepolymer that was suitable for the following SSP, the bulk MP of L-lactic acid was traced with 0.7 wt% of DBSA as the catalyst at 150 °C. Fig. 2.3 shows the time-dependent changes in M_w and *OP* of the PLLA oligomers formed during the bulk MP.

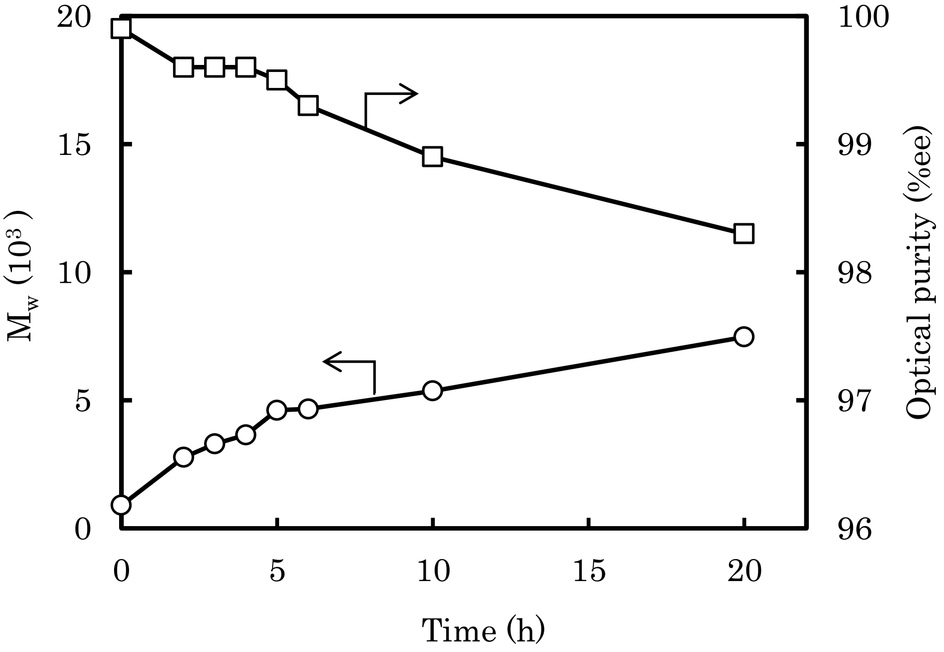

Fig. 2.3. Changes in molecular weight (○) and optical purity (□) of PLLA as a function of reaction time in the MP with DBSA as the catalyst (0.7 wt% relative to L-lactic acid).

It became evident that the M_w of the PLLA oligomer rapidly increases up to 5,000 Da within 5 h and gradually increases thereafter while the *OP* decreases slightly but continuously with the reaction time. The slowed acid-catalyzed MP after 5 h may be due to the lowered concentration of the end groups (carboxyls and hydroxyls) as well as to the decreased polarity of the reaction system with it. The gradual but continuous decrease in *OP*, on the other hand, may be attributed to the carbonyl activation by protonation that is likely to cause the racemization of the neighboring carbon atom. It was therefore concluded that the MP must be finished as early as possible to obtain a highly optically pure prepolymer that can readily crystallize before its subjection to SSP. The PLLA prepolymer ought to have an enough high molecular weight and a high T_m so as to retain solid-state at significantly higher temperatures of SSP (close to 140 °C). Based on the results of Fig. 2.3, it was decided to stop the MP at a reaction time of 3 h where the prepolymer had a M_w higher than 3,000 Da and an *OP* over 99.5 %ee. The prepolymer obtained in this particular run showed a T_m at 136 °C with a M_w of 3,300 Da and an *OP* of 99.6 %ee. Since the repeated MP gave a similar prepolymer with a M_w of c.a., 3,000 Da, it was subjected to the next SSP.

2.4.2. Solid-state Polycondensation

The SSP was conducted in reference to the procedure previously reported by Moon et al. [11]. After the MP mentioned above, the PLLA prepolymer with a M_w of about 3,000 Da was quenched to obtain a glassy product. Its DSC analysis indicated a broad exotherm around 100 °C and a broad melting endotherm around 130 °C due to the crystallization and the following crystal fusion, respectively. The latter endotherm ranged from 110 to 150 °C due to the presence of a variety of low-molecular-weight components. Therefore, the glassy prepolymer was annealed before starting the SSP by gradually increasing the temperature from 80 to 110 °C in 2.5 h. This temperature range was slightly lower than that of the initial melting of the PLLA prepolymer having a high *OP*. After this annealing, the thermal fusion of the solid PLLA prepolymer could be avoided in the following stage of SSP. The DSC thermogram of the annealed prepolymer revealed a sharper melting endotherm with loss of the crystallization exotherm having been observed before. The crystallinity estimated from the melting endotherm reached over 40 %. Since the annealed prepolymer maintained its solid-state above 120 °C, its SSP was started by heating it at 120 °C for 5 h, and then the temperature was stepwise raised up to 140 °C.

Fig. 2.4 depicts the typical time courses of M_w, *OP*, and crystallinity of the PLLA polymers produced during the annealing and SSP where the temperature program is shown by the dashed arrows.

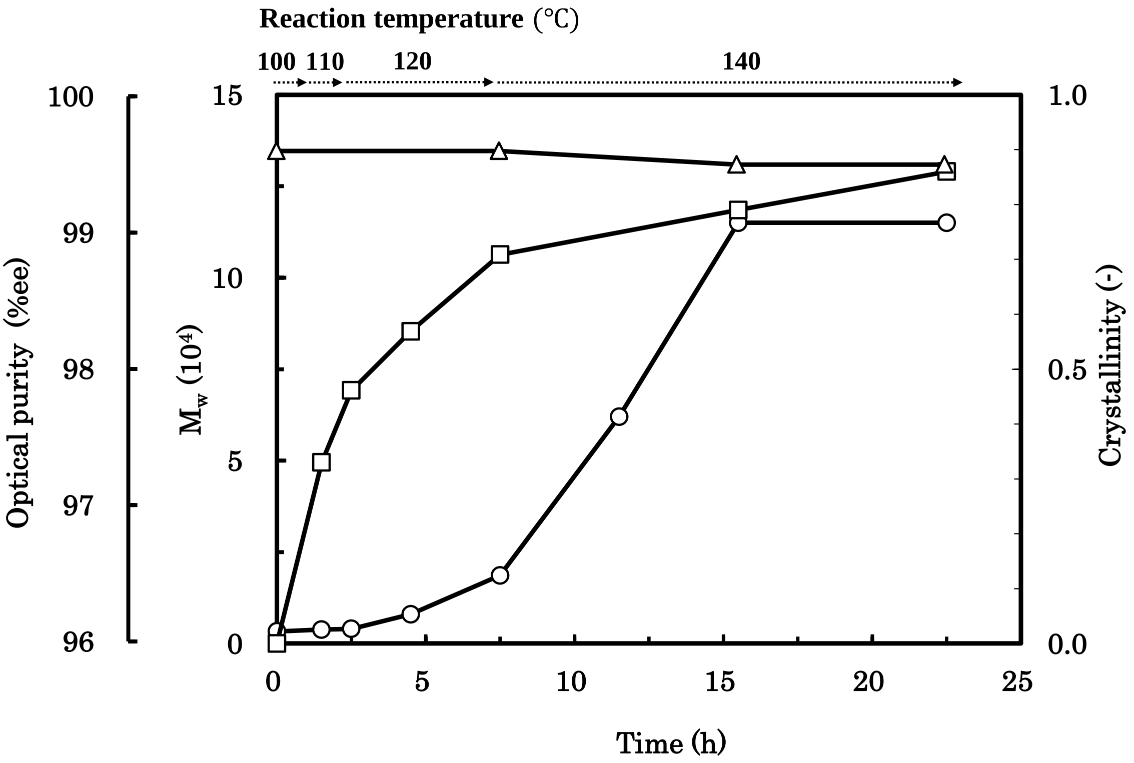

Fig. 2.4. Changes in M_w (○), *OP* (Δ), and crystallinity (□) of the PLLA polymers as a function of reaction time in the annealing and SSP. The dashed arrows indicate the time-dependent change of the reaction temperature.

In the early stage of SSP at 120 °C, the M_w increased from 4,000 Da to 18,500 Da, making the crystallinity of the PLLA polymer higher. When the following SSP was conducted at 140 °C, the M_w sharply increased to 115,000 Da within 8 h. However, further increase in the reaction time at 140 °C did not much increase the M_w. It was therefore evident that the increasing behaviors of the crystallinity and M_w of the PLLA polymer are different from each other. Namely, the crystallinity grew up quickly from 0% (amorphous) to 46% after annealing at 110 °C (Fig. 2.4), reached 71% in the early stage of SSP at 120 °C, and plateaued thereafter. On the other hand, the increase in M_w was the highest at the plateauing stage of the crystallinity, i.e., the second SSP stage (at 140 °C for 8 h). The crystallinity was 79% when the M_w reached the highest (115,000 Da). These results revealed that the significant increase in M_w took place in the highly crystalline state of the prepolymer obtained after the annealing and the initial stage of SSP at 120 °C. The relatively low M_w finally obtained in the present study may be due to the different catalyst system added here. Moon et al. used $SnCl_2$/p-TSA system which is more active than DBSA, makes the M_w reach the highest level [11]. DBSA, on the other hand, has only Bronsted acid activity and gives the ordinary level of M_w.

In the previous studies, some discrepancies have been encountered in interpreting the relation between the increases in crystallinity and M_w of PLLA polymer during the SSP. Several papers reported that the highly crystalline state of the prepolymer may likely decrease the reaction rate of SSP due to the decreased diffusivity of byproduct (condensed water) and chain mobility (terminal reactivity) [42,43]. The other reports indicated that the M_w ought to increase with increasing the crystallinity [25,26]. Duh studied how the crystallinity should affect the SSP rate in conjunction with the diffusivity of byproducts [25,27]. He proposed that the increase in crystallinity ought to result in increased concentration of the end-groups in the amorphous domain because of their segregation from the crystal domain, thereby increasing the probability of collision and reaction of the end groups. He consequently concluded that this positive effect outweighs the above negative effect by crystallization such as the decreased diffusion of byproducts and chain mobility. The present data in this chapter are compatible with this proposition. It was previously reported in the similar SSP of PET that the SSP rate decreases with increasing the crystallinity [42,43]. This fact may be because the diffusion resistance against the byproducts should be excessively high as the particle size of the reactant PET prepolymer is about 7 mm and greatly beyond a critical value. Such a negative effect owing to the decreased byproduct diffusivity could be neglected in present study where the particle size of the PLLA prepolymer was much smaller and less than 150 μm in diameter. As for the change in *OP* of the PLLA polymers, the initial *OP* value over 99.5 %ee observed for the PLLA prepolymer was almost kept throughout the whole process of annealing and SSP. It was therefore assured that racemization can be suppressed in the solid-state where the chain mobility is lower than in melt state and that the crystalline state of the PLLA prepolymer can be preserved in high degree even at the high temperatures of annealing and SSP.

Fig. 2.5 compares the WAXD profiles of the PLLA polymers obtained during the annealing and SSP. Each of these profiles supported the formation of α-form crystals in the whole stage of annealing and SSP. Even the annealed prepolymer consisted of α-form crystals instead of the α'-form that is often generated in the ordinary crystallization of PLLA. This may be because both the PLLA prepolymers and polymers retained high *OP* values, favoring the formation of the more perfect crystals (α-form).

As shown in Fig. 2.6, the T_m of the PLLA polymers increased with increasing the reaction time, reaching 180 °C in the final stage. It was therefore suggested that the crystalline structure of PLLA polymers grew more perfect in spite of little increase in crystallinity with the progress of SSP.

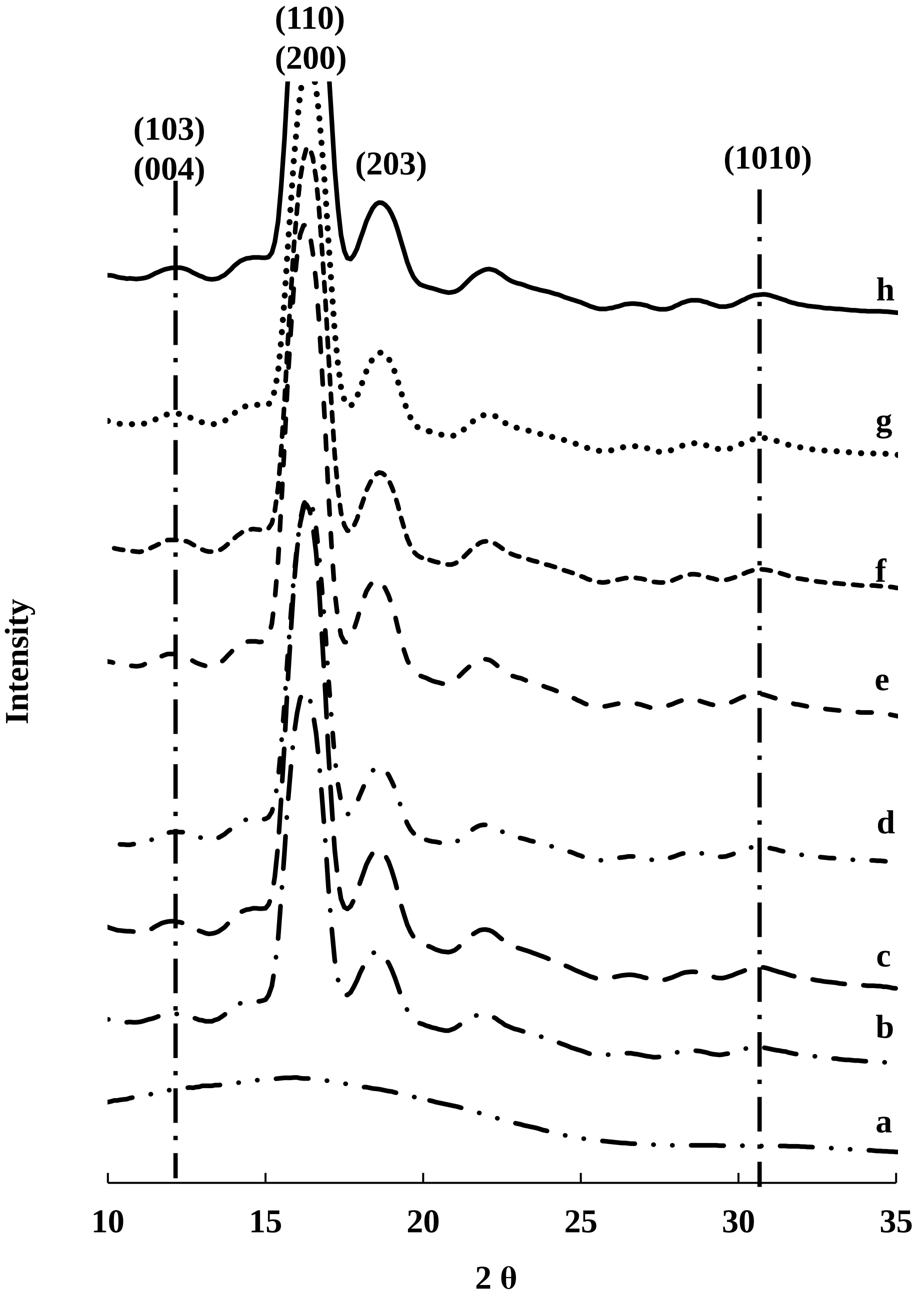

Fig. 2.5. WAXD profiles of the PLLA polymers obtained at different reaction stages (annealing and SSP); a: pre-polymer, b: 80 °C, c: 110 °C, d: 120 °C-2 h, e: 120 °C-5 h, f: 140 °C-4 h, g: 140 °C-8 h, h: 140 °C-15 h.

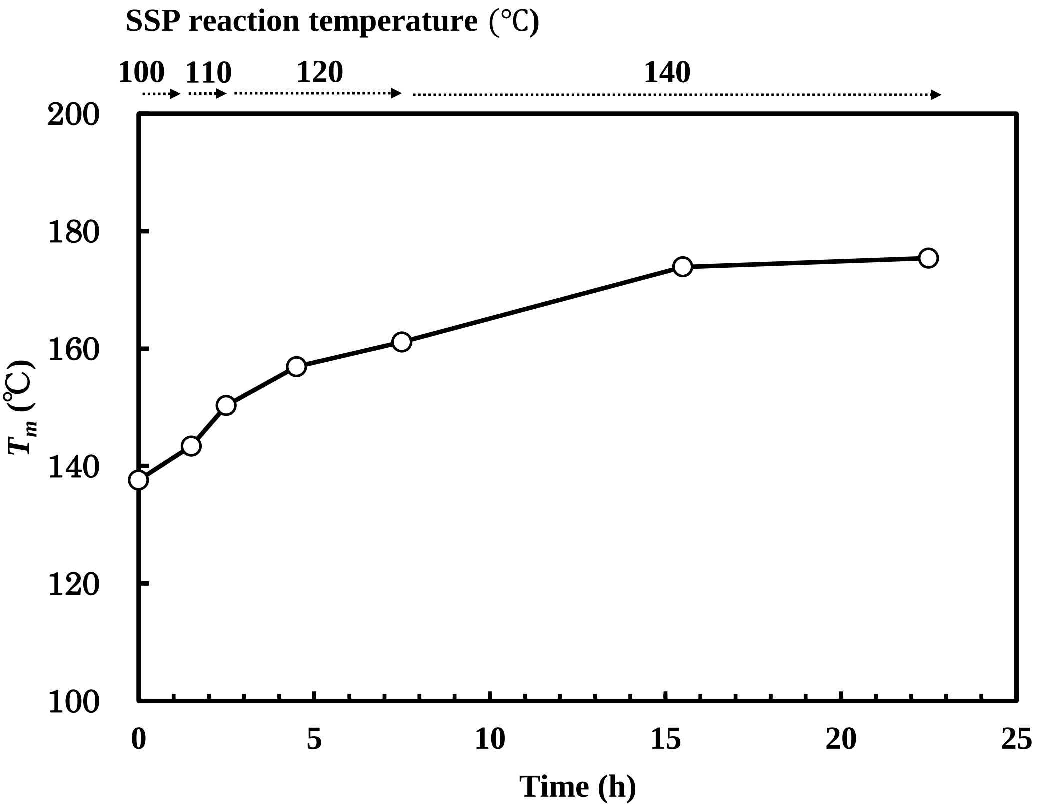

Fig. 2.6. Change in T_m of the PLLA polymers as a function of the reaction time in the SSP (annealing and SSP). The dashed arrows indicate the time-dependent change of the reaction temperature.

2.4.3. Effect of Crystal Morphology

Fig. 2.7 shows the Lorentz-corrected SAXS curves of the PLLA polymers obtained during the annealing and SSP. The values of long period (L), crystalline lamellar thickness (l_c), and amorphous layer thickness (l_a) were calculated from the curves by using one-dimensional correlation function as illustrated in Fig. 2.8.

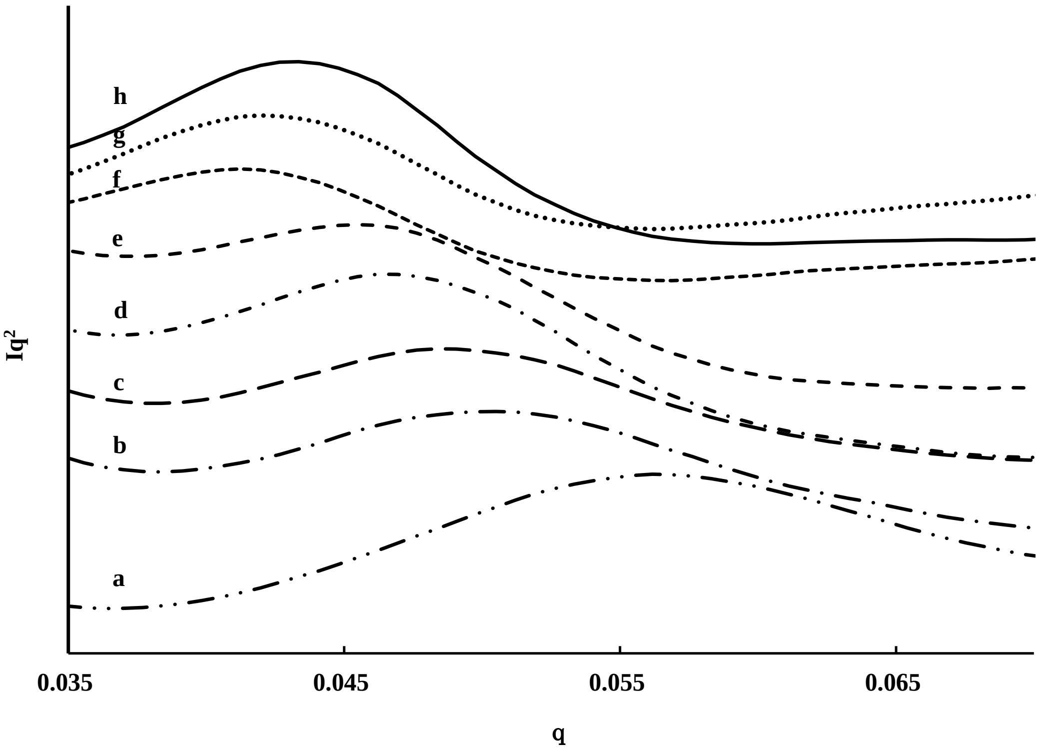

Fig. 2.7. Lorentz-corrected SAXS curves of the PLLA products obtained at different conditions, a: 80 °C, b: 100 °C, c: 110 °C, d: 120 °C-2 h, e: 120 °C-5 h, f: 140 °C-4 h, g: 140 °C-8 h, h: 140 °C-15 h.

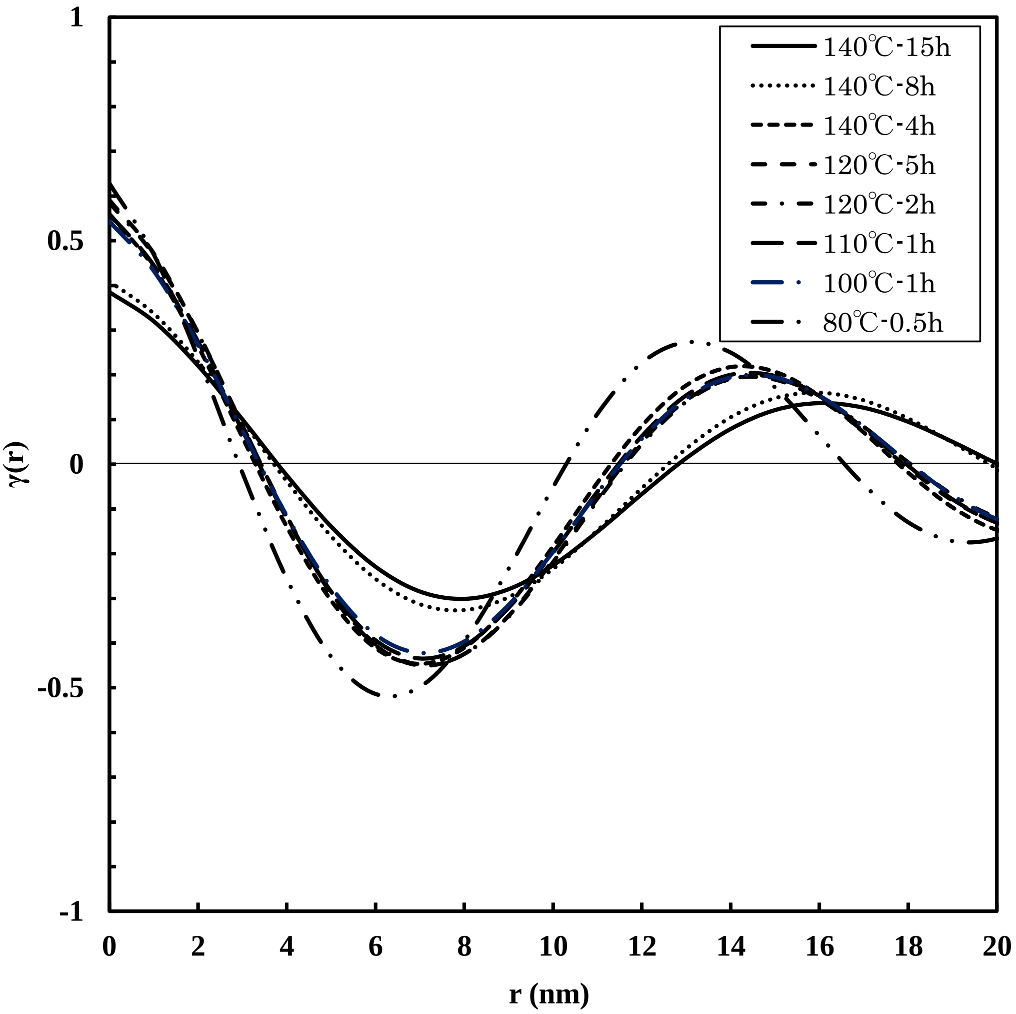

Fig. 2.8. One-dimensional correlation function profiles for the PLLA polymers obtained at different reaction conditions

The *L* values estimated from the equation $L_{(qmax)}$ = 2pai/qmax as well as the linear crystallinity (*wc*) are listed in Table 2.1. Before discussing these values, it is necessary to note which of l_1 or l_2 can be assigned to l_c on the one-dimensional correlation function. As mentioned earlier, the correlation function method cannot distinguish which thickness value can be caused by crystalline phase. There are two approaches for assigning l_1 or l_2 as l_c. One is inclined to assign the smaller value of l_1 and l_2 as l_c by assuming that the product of L and bulk crystallinity (X_c from WAXD or DSC) is closed to the lower value, i.e., $L \cdot X_c \cong \min(l_1, l_2)$. Such an assignment suggests that the polymer morphology consists of space-filling lamellar stacks. The other is to assign the larger value of l_1 and l_2 as $l_{c.}$ In semi-crystalline polymers with semi-stiff chains such as PET, poly(butylene terephthalate) (PBT), and polyether ether ketone (PEEK), the lamellar stacks commonly formed in the space-filling spherulites cannot fill up the entire space of the spherulites because there should be a broad amorphous gap between the lamellar stacks. The assignment of $l_c = \max(l_{1,}\ l_2)$ must accordingly be rationalized by conforming the correct relation between the bulk crystallinity and the linear crystallinity calculated by $wc = (l_c / L)$ ($\max(l_1, l_2)$ as l_c). When $l_c = \min(l_1, l_2)$ based on the first morphology model consisting of space-filling lamellar stacks in spherulites were assigned, the M_w of the polymer ought to continuously increase during the SSP. However, such increase in M_w was not confirmed after M_w had reached over

115,000 Da. Thus, we decided to adopt the second morphology model assuming l_c = max (l_1, l_2) in this chapter.

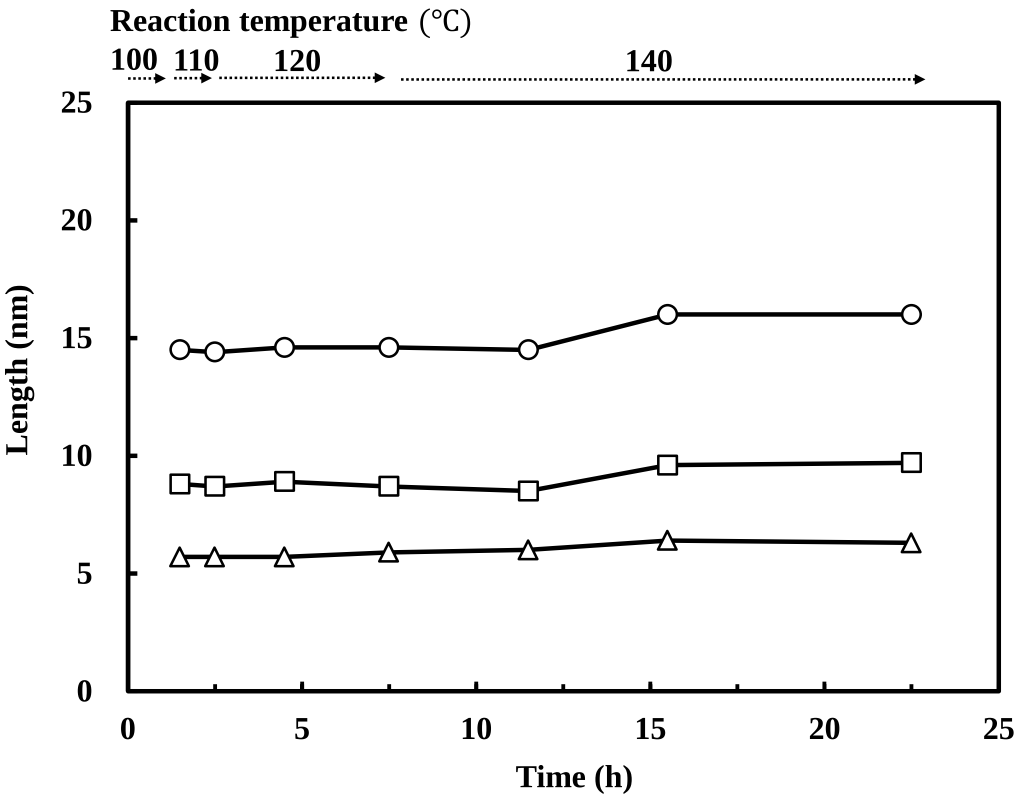

Fig. 2.9. Time-dependent changes in long period, *L* (○) and thicknesses of crystalline, l_c (□) and amorphous, l_a (Δ) layers of the PLLA polymers in the annealing and SSP. The dashed arrows indicate the time-dependent change of the reaction temperature.

As illustrated in Fig. 2.9, the *L*, l_a, l_c, and *wc* values were practically constant throughout the whole stages of annealing and SSP. Furthermore, no other new explicit peak attributable to different crystal forms was observed during the reaction. These results mean that the lamellar morphology did not much change and that the polymer chains elongated by the SSP were little involved in crystallization between the lamellar crystals. As discussed earlier, the prepolymer has been crystallized in the step of annealing and initial SSP below 120 °C, showing the increase in crystallinity from 0% (the amorphous state) to 71% as well as the growth of lamellar thicknesses L and l_c. In this stage, however, the increase in molecular weight was limited. Although the polymer end groups and catalyst ought to have concentrated in the amorphous domain by the polymer crystallization, their reaction for chain elongation may have been little enhanced because of the low reactivity below 120 °C. When the reaction temperature was elevated up to 140 °C, the increase in M_w has become evident with little change in the crystalline morphology. Small shrinkage of l_a must be observed considering the loss of condensation products during the polycondensation. However, this shrinkage ought to be in an undetectable level because the polycondensation reaction should mainly occur among the adjacent molecular end groups existing on the (001) planes of crystal lattices (vide infra). Considering the distribution in L and l_c, the changes in l_a and l_c may be within the experimental error. The increased L value above 16 h in reaction time may suggest that the crystal growth has been induced by the preferential growth of the smaller or thinner crystal lattices during the SSP.

Table 2.1 compares the M_w of the PLLA polymers obtained at 130 and 140 °C. The final M_w obtained at 130 °C was significantly lower than that obtained at 140 °C in spite of the similar crystalline morphology between the two series.

Table 2.1. Lamellar crystal data obtained from the equation $L_{(qmax)}$ = 2pai/q_{max} and linear crystallinity *wc* of the PLLA polymers prepared by SSP.

Reaction Temp. (°C)	Time (h)	M_w	X_c	T_m (°C)	$L_{qmax}{}^{a}$ (nm)	L^b (nm)	$l_a{}^b$ (nm)	$L_c{}^b$ (nm)	wc^c
140	15.5	11.5	0.79	173.9	13.9	16	6.4	9.6	0.6
	22.5	11.5	0.86	175.4	13.4	16	6.3	9.7	0.6
130	15.5	7.0	0.77	170.7	13.9	14.5	5.7	8.8	0.6
	22.5	8.6	0.77	171.4	13.9	14.5	5.7	8.8	0.6

[a] Determined from the Lorentz-corrected SAXS curves

[b] Determined by one-dimensional correlation function profile

[c] Calculated by l_c / L

Still, an important question remains: which part of the amorphous domain is involved in the chain elongation reaction after the crystal evolution, inside or outside the lamellar? As seen in the time course of M_w at 140 °C, M_w did not much increase after reaching 115,000 Da. If the chain elongation reaction should take place in the amorphous domain outside lamellae, the increase in M_w would not retard because the end groups can come across the lamellae in spherulites for continuation of the chain extension. If the chain elongation reaction should take place in the amorphous layers inside the lamella, a restricted number of end groups must be involved in the reaction for chain extension. The latter situation can better explain the limited increase in M_w during the SSP because the end groups inside the lamellar ought to more easily come across with their neighboring end groups sitting within a mobile radius to incur the chain elongation reaction than those randomly placed outside the lamellar. If so, the crystal morphology ought to be closely related with the chain elongation of the PLLA polymer.

As noted by the WAXD profiles (Fig. 2.5), the crystal structure of the PLLA polymers conformed to the α-form in the whole stage of annealing and SSP. Since the α-form consists of pseudo-orthorhombic unit cells (a = 1.078 nm, b = 0.604 nm and c (molecular axis) = 2.78 nm) containing two polymer chains having a 10_3 helical conformation in the unit cell [44], the stacking direction of crystalline lamella is in the direction of c axis of the unit cell. The crystalline lamellar thickness (l_c) in this c axis direction only slightly increased from 8.7 nm noted after the annealing (110 °C) to 9.8 nm after the SSP (16 h at 140 °C) as noted in Figure 2.9. The former l_c (8.7 nm), being almost three times the c axis length of a unit cell or the unit helical length, corresponds to the length of an α-form helical chain (10_3 helix) composed of 35 lactic acid units with an M_n of 2,500 Da. Namely, the helical chains having around 9 nm in c axis length align in the a and b directions (as detected by the WAXS peaks from the (110) and (200) planes) to form a crystalline lamella. This crystalline lamella is sandwiched by amorphous layers to form lamellar crystals. The whole process of this lamellar formation has been completed during the annealing below 110 °C. Since the terminal groups and the segmental short chains connecting with the crystal chains should be placed in the amorphous layers, they ought to readily interact with each other, particularly, on the surface of ab planes of the crystalline layers. This interaction can cause the acid-catalyzed condensation reaction above 120 °C to lead the chain elongation up to 140 °C, bringing the slight increase of crystalline layer thickness. Since the alignment of the helical chains of PLLA in the crystalline lamella may be uncertain, the heads (hydroxyl) and tails (carboxyl) of the chains ought to be arranged randomly on the ab surface of the crystalline lamella, and some of the head and tail functional groups are likely to remain unreacted to limit the increase in molecular weight of the PLLA polymers (Fig. 2.10).

It is therefore deduced that the final molecular weight obtained after the SSP should depend on the crystal morphology of the annealed samples or how orderly the helical chains of the precursory PLLA oligomers are arranged in the lamellar crystals that are formed in the crystallization step. The slowing down of increase in molecular weight in the later stage of SSP can also be explained by the enhanced restriction of the segmental motion induced by the increase of the molecular weight in which the active chain ends are partly "buried" within the polymer chain networks to lose reactivity. The contribution of these effects has remained unknown here.

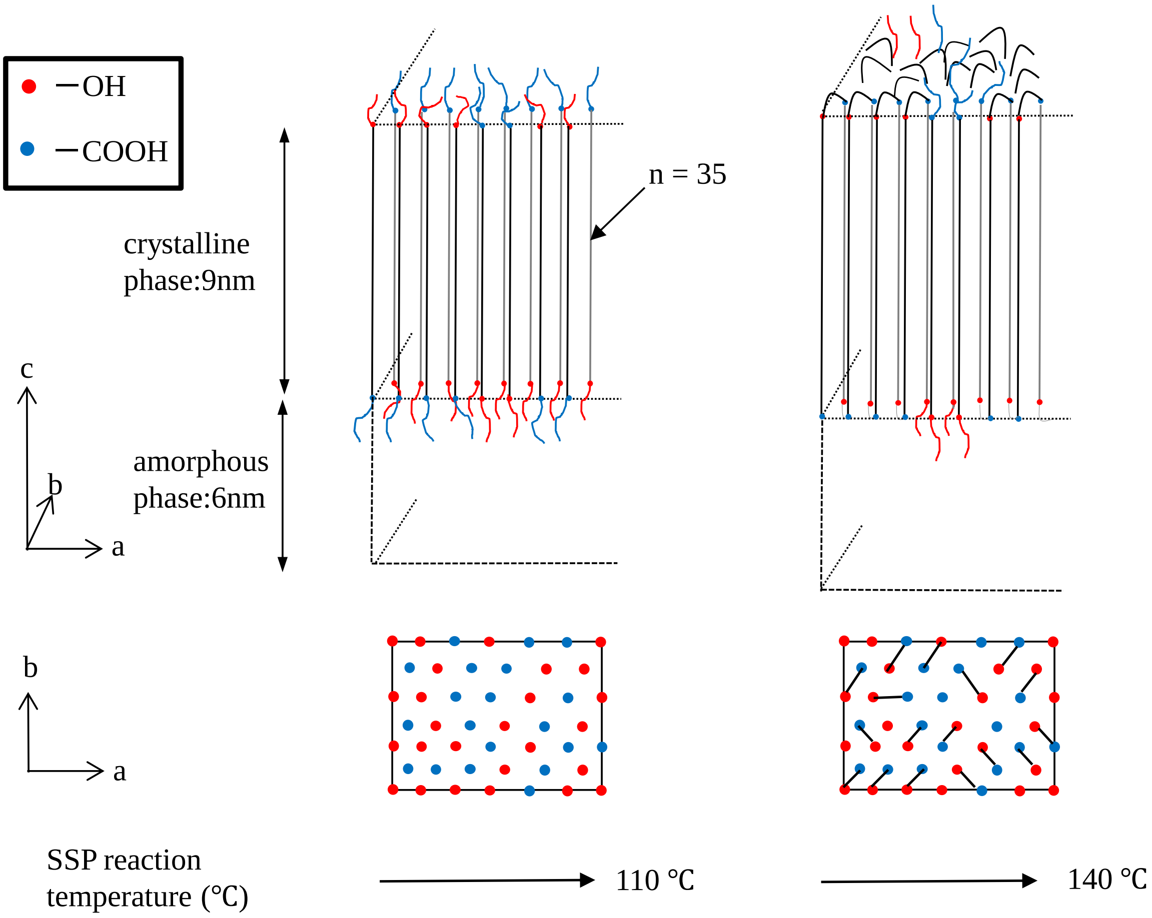

Fig. 2.10. Chain-terminal reactions on the ab planes of the crystal lamella of PLLA during SSP.

2.5. Conclusion

A PLLA prepolymer having a M_w of c.a., 3,000 Da and a high *OP* over 99 %ee was prepared by bulk MP of L-lactic acid with dodecylbenzenesulfonic acid as the catalyst. It was then annealed at 80–110 °C for its crystallization and subjected to SSP in which the M_w of the PLLA polymer became higher than 100,000 Da with increasing the SSP temperature stepwise from 120 to 140 °C. The highest increase in M_w was observed at 140 °C, while the crystal growth of the PLLA polymer was induced in the annealing and the early stage of SSP at 120 °C before the increase in molecular weight. It was found out that the PLLA polymer retained the α-form crystal throughout the annealing and SSP with little change in lamellar morphology. It was therefore suggested that the polycondensation of the terminal groups of the PLLA prepolymer is more highly induced in the amorphous domain inside the crystal lamellae than in the amorphous domain outside the crystal lamellae. Since the terminal groups and segmental short chains of the PLLA prepolymer are placed on the surface of the ab planes of the crystalline layers in the lamellae, they ought to readily interact with each other to cause the acid-catalyzed condensation reaction above 120 °C and lead the chain elongation (up to 140 °C) with slight increase in thickness of crystalline layers. Therefore, the crystal morphology of the annealed samples should be important for increasing the final molecular weight of PLLA in the SSP. A well oriented state of the helical chains of the

PLLA prepolymer must be realized in the crystallization step for obtaining a high-molecular-weight PLLA.

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Chapter 3

Influence of Decomposition Temperature of Aromatic Sulfonic Acid Catalysts on the Molecular Weight and Thermal Stability of Poly(L-lactic acid) Prepared by Melt/Solid-State Polycondensation

3.1. Introduction

Poly(L-lactic acid) (PLLA) is a synthetic biodegradable polymer that can be prepared from renewable resource. It has been applied to wide variety of purposes because of its excellent physico-chemical properties and reasonable cost-property balance. PLLA is manufactured by multi-step processes, i.e., L-lactide monomer is prepared from L-lactic acid (LLA) via depolymerization step of PLLA oligomers, and it is purified and polymerized by ring-opening polymerization (ROP) [1–3]. This method is highly effective to obtain PLLA with high molecular-weight, although the synthetic process of L-lactide requires high energy consumption, making the PLLA product costly. Therefore, various attempts have been made in the past two decades to develop an alternative route [4–10], which is based on direct polycondensation of L-lactic acid. This route is considered to be more cost-effective than the conventional ROP route, although it is difficult to obtain high molecular weight of PLLA because of the unfavorable formation of cyclic oligomers and uneasy control of the dehydration/hydration equilibrium between ester and acid/hydroxyl groups. Until now, many researchers have claimed optimum polymerization conditions and catalysts for the direct polycondensation of lactic acid. Among them, Moon et al. disclosed a binary catalyst system composed of Sn(II) dichloride dihydrate/p-toluene sulfonic acid ($SnCl_2 \cdot 2H_2O$/TSA), with which a high-molecular-weight PLLA was readily prepared by melt-solid polycondensation (MP/SSP). In this catalyst system, the activity of Sn(II) is well controlled by protonic acid. It has accordingly been utilized as the most popular catalyst in the MP/SSP of PLLA [6,7]. However, the Sn(II) compound, showing toxicity, is hardly removed from the polymeric product, and the resultant PLLA containing the remaining Sn(II) should have limited use as medical, pharmaceutical, and agricultural materials. Furthermore, it has been reported that the remaining catalyst is likely to deteriorate the thermal stability of the polymeric products [11,12]. To solve this problem, various non-metallic catalysts that can easily be removed from polymeric products have been utilized in the SSP as the more desirable catalysts. Such non-metallic catalysts examined involved sulfonic acids, onium salts, organic acid anhydrides, ionic liquids, creatinine, and so on [13–17]. Bo Peng et al., for example, recently analyzed the relationship among the acidity of sulfonic acids, their miscibility with PLLA oligomer, and the thermal stability of the PLLA products in the MP/SSP [12]. They reported that PLLA with excellent thermal stability, high molecular weight, and least coloration can be obtained with 1,3-propanedisulfonic (PSA) acid and 1,5-naphtalene disulfonic (NSA) acid as the catalysts. However, further study was needed to clarify the influence of the properties of sulfonic acid catalysts on the molecular weight increase and thermal stability of the resultant PLLA, because in chapter 2, it was mentioned that their behavior is greatly affected by the desulfonation reaction of the sulfonic acid catalyst in the MP/SSP. In addition, the fate of the sulfonic acid catalysts ought to give a profound effect not only on the molecular weight change during the polymerization but also on the thermal annealing and melt-processing that are conducted at high temperature.

In chapter 3, several aromatic sulfonic acids having different number of alkyl substituents were examined as the organic catalysts of MP/SSP. Since they showed different thermal degradation behaviors at the temperatures of MP/SSP, their degradation was found to give strong influence on the degree of polymerization and thermal stability of the PLLA finally obtained. In this chapter, how the sulfonic acids can work as catalysts in the SSP and how they can be removed from the SSP products by their thermal annealing are described.

3.2. Materials and Methods

3.2.1. Materials

L-lactic acid (LLA, HiPure 90) containing 10 wt% of water was commercially supplied by Corbion Purac (Gorinchem, Holland). 2,4,6-Trimethylbenzenesulfonic acid (MSA) was purchased from Sigma-Aldrich Co. LLC (St. Louis, USA). 2,4-Dimethylbenzenesulfonic acid (m-XSA), 2,5-dimethylbenzenesulfonic acid (p-XSA), p-toluenesulfonic acid monohydrate (p-TSA) and dodecylbenzenesulfonic acid (DBSA) were purchased from Tokyo Chemical Industries, Co. Ltd. (Tokyo, Japan). PLLA samples, U'z® S-06 (M_w 18.9 × 10^4, M_w/M_n= 2.2) and LAYCIA® (M_w 13.8 × 10^4, M_w/M_n= 2.3) were purchased from Toyota Motor Co., Ltd. (Aichi, Japan) and Mitsui

Chemicals, Inc. (Tokyo, Japan), respectively. All these materials were used without purification.

3.2.2. Melt Polycondensation

Melt polycondensation (MP) to obtain a PLLA prepolymer was conducted as follows. L-lactic acid and a sulfonic acid (0.25 mol% amount relative to L-lactic acid) as a catalyst were charged into a flask and well mixed by mechanical stirring. The mixture was then heated at 150 °C under 30 mmHg for 3 h. The generated water was trapped in a cold vessel connected to a vacuum pump throughout the MP. A PLLA prepolymer having a molecular weight of several thousands and a melting temperature (T_m) around 110–150 °C was finally obtained. It was quenched in a cold bath for making it keep amorphous state.

3.2.3. Solid-state Polycondensation

The PLLA prepolymer obtained above was pulverized with an electrical mill (WB-1, Osaka Chemical Co., Japan) to a size less than 150 μm in diameter, and the resulting powders were divided into several test tubes. Each tube was annealed by increasing the temperature from 80 to 110 °C in a period of 2.5 h to make the powdery prepolymer crystallize and then heated at a predetermined temperature under 10 mmHg for a predetermined time to conduct SSP. The finally obtained product in powdery form was then analyzed.

3.2.4. Thermal Stability of Poly(L-lactic acid) Products

The PLLA products obtained above were subjected to thermal annealing at 220 °C for 30 min, and their molecular weight was measured by gel permeation chromatography (GPC). The molecular weight retention was calculated by the following formula.

Molecular weight retention = 100 × (M_w after annealing / M_w after SSP)

3.2.5. Extraction of Oligomeric Products from Obtained Poly(L-lactic acid) products

A portion of a PLLA product obtained above (0.5 g) was dispersed in an acetone (50 mL) for 30 min. Then, the acetone solution was separated by filtration and evaporated to dryness. The remaining extract was analyzed by ^{1}H NMR and MS spectra.

3.3. Measurements

Number- (M_n) and weight-average (M_w) molecular weights and dispersity (M_w/M_n) of PLLA polymers were determined by GPC on an apparatus (GL-7400, GL Science Inc., Japan) with a refractive index detector (GL-7454, GL Science Inc., Japan). A combination of three columns (Shim-pack® GPC-802C, 804C and 806C, Shimadzu Co., Japan) were used at 40 °C with chloroform as the mobile phase. Polystyrene (PS) standards were used to calibrate the relative molecular weights. The optical purity (*OP* in %ee) of the PLLA products was determined in the same manner as section 2.3.1. The melting temperature (T_m) of polymer samples was determined by DSC on a DSC-50 thermal analyzer (Shimadzu) at a heating rate of 10 °C/min.

Thermal gravimetric analysis (TGA) was conducted on an apparatus of TGA-2950 (TA Instruments, USA) in a temperature range from 23 to 400 °C at a heating rate of 10 °C/min to evaluate the thermal decomposition temperatures. All measurements were conducted under nitrogen atmosphere. ^{1}H NMR spectra were recorded on a spectrometer ARX-type (Bruker Co., USA) at 300 MHz. The content of an aromatic sulfonic acid in the resultant polymer was determined by the ^{1}H NMR signals in reference to those of an internal standard, 1,1,2,2-tetrachloroethane. Mass spectra (MS) of oligomeric extracts from the PLLA products were measured by LC-Mass spectra using an instrument of LCMS-Q8000 (Shimadzu). The MS measurement was carried out in the negative mode in the maximum mode of 1000 in mass number.

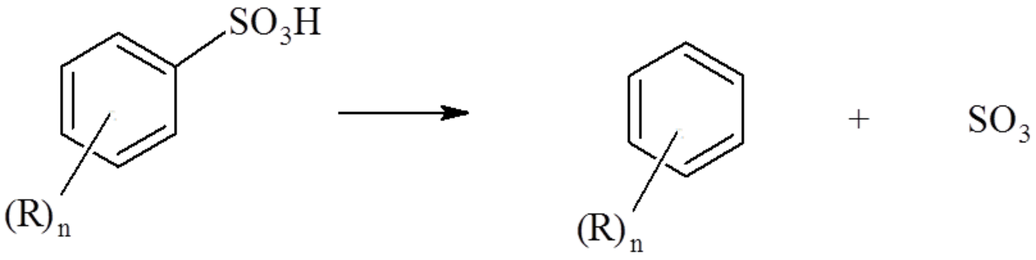
3.4. Results and Discussion

3.4.1. Aromatic Sulfonic Acid Catalysts

The direct polycondensation of PLLA catalyzed by various metal compounds have been extensively investigated in the past decades. Through these studies, stannous dichloride dihydrate combined with a sulfonic acid has been known as the most active catalyst in the polycondensation of PLLA [7]. However, several references reported that tin chloride remains in the product polymer, causing severe polymer decomposition under thermal melting and long-term storage [11,12]. Bo Peng et al. recently investigated the effects of residual tin catalyst on the thermal stability of PLLA and reported that the tin catalyst obviously deteriorates the thermal stability of PLLA [12].

Namely, they confirmed by their TGA analysis that the thermal stability is significantly different between the PLLA samples having residual tin catalyst in about 2000 ppm and almost 0 ppm. This may be because the tin catalyst should likely cause depolymerization of PLLA into lactide by back-biting side reaction. They also found out that organic sulfonic acids could be effective catalysts that do not lower the thermal stability of PLLA [12]. They used TSA and PSA, for example, which showed enough thermal stability, acidity, and high compatibility with LLA to achieve both high catalytic activity and least decomposition of polymeric products.

Polycondensation of lactic acid is actually an esterification reaction of the carboxyl and hydroxyl groups, which is catalyzed by aromatic sulfonic acids. It is known that these sulfonic acids decompose without vaporization as soon as the water is removed from their hydrate state. (Scheme 3.1) [18].



Scheme 3.1. Decomposition of an aryl aromatic sulfonic acid.

Their decomposition temperature varies depending on the type of substituents on the aromatic ring. Fig. 3.1 shows the thermal decomposition behaviors of a series of aromatic sulfonic acids having different numbers of alkyl substituents. It is indicated that the thermal decomposition became quantitative above 200–300 °C in each sulfonic acid.

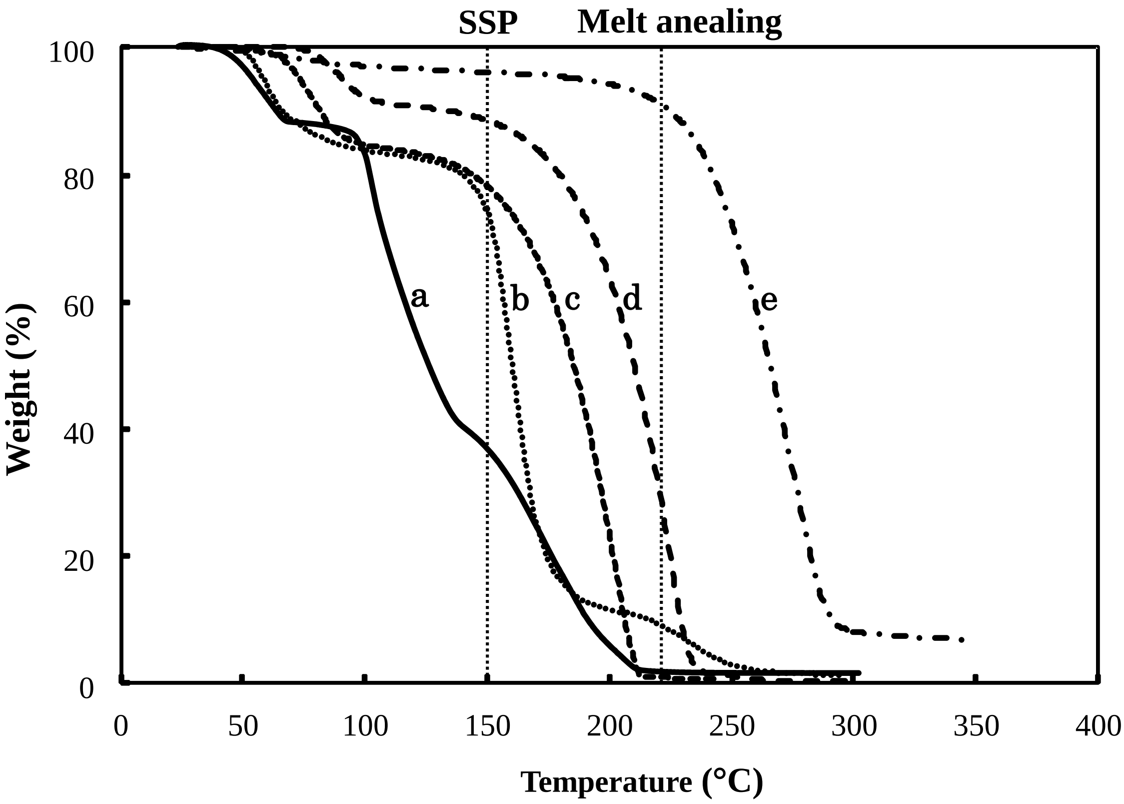


Fig. 3.1. TGA profiles of aromatic sulfonic acid catalysts; a: MSA, b: m-XSA, c: p-XSA, d: p-TSA, e: DBSA. The two dotted lines show temperatures at which SSP and melt-annealing were done.

The thermal decomposition temperature of sulfonic acids was evaluated by the temperature showing 5% weight loss ($T_{d,5\%}$) after the initial weight loss accompanied by the removal of moisture below 100 °C. This $T_{d,5\%}$ value was found to decrease with increasing the number of methyl groups that are electron donating groups, with a decreasing order of TSA > XSA > MSA (Table 3.1). In addition, the thermal decomposition behavior of XSA varied depending on the substitution position of the phenyl ring: m-XSA > p-XSA. The chain length of the alkyl groups also affected the decomposition, and DBSA having a long alkyl chain length showed the highest $T_{d,5\%}$. Consequently, the decomposition of the selected five sulfonic acids increased in an order of MSA > m-XSA > p-XSA > p-TSA > DBSA.

Table 3.1. pKa and $T_{d,5\%}$ of aromatic sulfonic acids

Catalyst	Alkyl group	Alkyl position	Number of alkyl groups	pKa	$T_{d,5\%}$[a]
MSA	Methyl	ortho, meta, para	3	-1.75	101
m-XSA	Methyl	ortho, para	2	-	146
p-XSA	Methyl	ortho, meta	2	-1.94	155
p-TSA	Methyl	Para	1	-2.14	177
DBSA	Dodecyl	Para	1	-1.84	228

[a] Thermal decomposition temperature of 5 wt% weight loss after dehydration.

3.4.2. Melt/Solid-state Polycondensation of Poly(L-lactic acid) Catalyzed by Aromatic Sulfonic Acids

Melt/solid-state polycondensation of LLA was carried out as reported before by using the above aromatic sulfonic acids as the catalysts [8]. When the MP was continued for long time, the molecular weight of PLLA increased to a level of 10^4, becoming 1.3×10^4 Da and 0.7×10^4 Da in M_w with MSA and DBSA as the catalysts, respectively, at a reaction condition of 150 °C for 20 h. In chapter 2, it had shown that in the MP the optical purity (*OP*) of the produced PLLA decreases with polymerization time and that the increase in molecular weights slows down after it reaches 0.5×10^4 Da. In this chapter, therefore, the MP was stopped after 3 h passing. The results of the MP with the sulfonic acid catalysts are summarized in Table 3.2. The molecular weight of the PLLA polymer obtained MSA was the highest, being more than 1000 Da higher than that of the PLLA polymers obtained with other catalysts. p-XSA, p-TSA, and DBSA gave similar molecular weights, which may be because the auto-catalytic polycondensation was more dominant than the sulfonic acid-catalyze reaction in the MP process. The appearance of the obtained polymers also depended on the catalyst.

m-XSA, p-XSA, and TSA gave transparent products, whereas MSA and DBSA gave slightly yellowish products. The polymer prepared with MSA was the most highly discolored. The DSC curves of the PLLA products indicated broad exotherm and endotherm around 100 °C and 130 °C due to the crystallization and the following crystal fusion, respectively. The latter endotherm ranged from 110 to 150 °C due to the presence of a variety of low-molecular-weight components.

In order to further increase the molecular weight, the powdery polymers obtained by MP were subjected to thermal annealing and SSP. The annealing was first performed at 100 °C for 2 h to make the polymers crystallize to prevent fusion of the powdery polymers. After confirming that the crystallization peak had disappeared with the melting peak becoming sharp by DSC, the SSP was conducted at 120 °C for 5 h and further at 150 °C for 15 h. The results of this SPP are summarized in Table 3.2. With each catalyst, the molecular weight of the SSP products remarkably increased, being higher than 10^5 Da with almost unimodal dispersity.

Table 3.2 Results of MP/SSP of PLLA catalyzed by various aromatic sulfonic acids.

Catalyst	MP[a]			SSP[b,c]				
	M_w (10^4) 150 °C-3 h[a]	M_n (10^4) 150 °C-3 h[a]	Color	M_w (10^4) 120 °C-5 h[b]	M_n (10^4) 120 °C-5 h[b]	M_w (10^4) 150 °C-15 h[c]	M_n (10^4) 150 °C-15 h[c]	Color
MSA	0.5	0..2	Pale yellow	4.2	1.6	14.5	5.7	Pale yellow
m-XSA	0.4	0.2	White	3.1	1.4	13.1	5.7	White
p-XSA	0.4	0.2	White	1.9	0.9	11.9	5.5	White
p-TSA	0.4	0.2	White	2.2	1.1	11.1	5.2	White
DBSA	0.4	0.2	Pale yellow	1.7	0.8	13.3	5.6	Pale yellow

[a] Melt polycondensation at 150 °C under 30 Torr for 3 h.

[b] Solid-state polycondensation at 120 °C under 10 Torr for 5 h.

[c] Solid-state polycondensation at 150 °C under 10 Torr for 15 h.

[d] The optical purity measured by HPCL was 99 %ee for all the polymer

As discussed above, the esterification cannot easily proceed in the MP process because the concentrations of the catalyst and polymer terminals are low. On the other hand, as crystallization proceeds in the SSP, both the polymer terminals and catalysts are concentrated in the amorphous region to enhance the esterification reaction [7]. Thus, the molecular weight increase becomes evident in the SSP process, although the polymerization temperature is not so high as to keep the solid-state. Among the sulfonic acids examined, MSA exhibited the highest catalytic activity even in the SSP, and the molecular weight reached 14.5×10^4 Da. The increasing order of molecular weight of PLLA after the SSP was: MSA > m-XSA > DBSA > p-XSA, p-TSA, which was opposite to the order of acidity of sulfonic acids: p-TSA > XSA > DBSA > MSA but not correlating to the decreasing order of thermal decomposition temperature: DBSA > p-TSA > p-XSA > m-XSA > MSA. The former relation between the molecular weight increase and the catalyst properties will be discussed in later section. Even when the reaction time was prolonged to 15 h or more, no further increase in molecular weight was recorded with any catalyst system. Note that neither reduction of optical purity nor remarkable increase in coloration were observed during SSP. The DSC profiles in the 2nd run showed a similar T_m (170 °C) for all the polymers

3.4.3. Thermal stability of PLLA prepared with aromatic sulfonic acid catalysts

The PLLA polymers obtained by the SSP were dried to remove moisture and then kept at 220 °C for 30 min to evaluate their thermal stability by the changes in molecular weight and appearance (Table 3.3). The molecular weight decrease was found to differ depending on the catalyst involved in the polymers, being in an order of: p-XSA > p-TSA > m-XSA > DBSA ~MSA. Little decrease in molecular weight was noted even after melting at 220 °C for p-XSA and TSA catalysts and for which the retention of the molecular weight with respect to the initial molecular weight was over 70 %. In addition, the appearance of these polymers obtained with p-XSA and p-TSA catalysts did not change after the melting and kept a substantially transparent state, showing the same thermal stability as that of PLLA polymers obtained by the lactide method. On the other hand, in the polymers obtained with MSA and DBSA catalysts, the molecular weight remarkably decreased after the melting at 220 °C to reach 30 % in the retention of molecular weight.

Table 3.3 Molecular weight of PLLA catalyzed by aromatic sulfonic acids after melting at 220 °C

Catalyst	M_w (10^4)[a] Initial	M_n (10^4)[a] Initial	M_w (10^4)[b] 220 °C-0.5 h	M_n (10^4)[b] 220 °C-0.5 h	M_w retention[c] (%)	Color	Amount of acetone extract (%)[d]
MSA	14.5	5.7	4.0	2.0	27.6	Dark brown	0.49
m-XSA	13.1	5.6	8.7	3.9	66.4	Clear	0.89
p-XSA	11.9	5.5	9.7	4.3	81.5	Clear	0.46
p-TSA	11.1	5.2	7.9	3.9	71.2	Clear	0.76
DBSA	13.3	5.6	4.3	2.2	32.3	Dark brown	4.10
MSA (washed)[e]	15.2	6.0	11.7	5.0	77.0	Slightly brown	nd
DBSA (washed)[f]	13.9	5.6	11.2	4.5	80.6	Clear	nd
$SnCl_2$/p-TSA[g]	19.7	6.4	2.1	0.8	10.7	Dark brown	nd
(U'z® S-06)[h]	18.9	8.5	15.7	7.0	83.1	Clear	nd
(LAYCIA®)[i]	13.8	5.0	9.7	3.9	70.3	Clear	nd

[a] Molecular weight of PLLA after the SSP at 150 °C under 30 Torr for 3 h.

[b] Molecular weight of PLLA after melting at 220 °C for 0.5 h.

[c] M_w of PLLA after the melting relative to the initial M_w of PLLA.

[d] The amount of acetone extracts relative to the amount of PLLA.

[e] A PLLA sample prepared with MSA catalyst was washed with acetone.

[f] A PLLA sample prepared with DBSA catalyst was washed with acetone.

[g] Prepared by the MP/SSP with a catalyst amount of 0.5 wt% relative to lactic acid.

[h] A commercial PLLA supplied by TOYOTA Motor Co., Ltd.

[i] A commercial PLLA supplied by Mitsui Chemicals, Inc., Ltd.

Also, the color change was remarkable, and the initial pale yellowish appearance turned to dark brown. These results indicated that the residual sulfonic acid induced hydrolysis and intermolecular transesterification, causing remarkable decrease in molecular weight and discoloration in the melting process at 220 °C.

Based on the data shown in Tables 3.2 and 3.3, the maximum M_w of PLLA reached after the SSP and the M_w retention after the melting process at 220 °C for 0.5 h are plotted as a function of $T_{d,5\%}$ of sulfonic acids in Fig. 3.2 and 3.3, respectively.

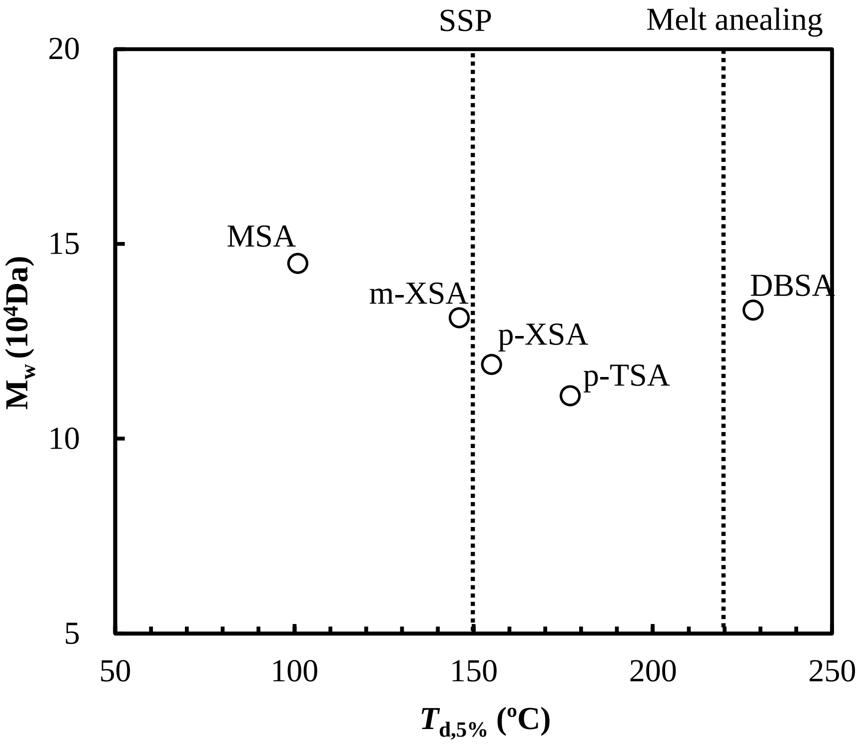


Fig. 3.2. Molecular weight of PLLA reached after SSP vs. $T_{d,5\%}$ of aromatic sulfonic acid catalysts.

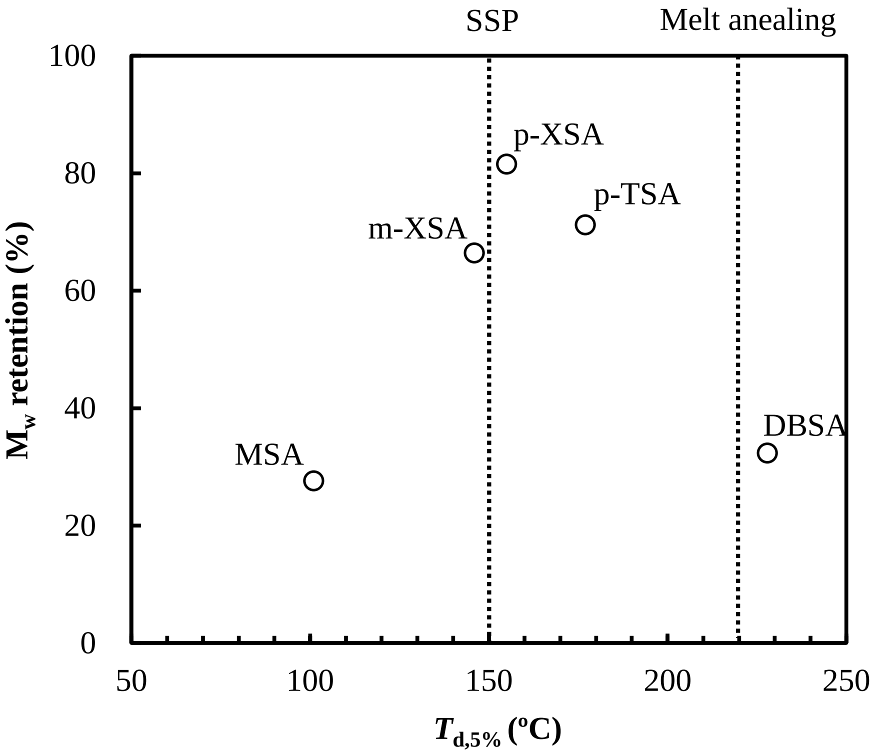


Fig. 3.3. Molecular weight retention of PLLA obtained after thermal annealing vs. $T_{d,5\%}$ of aromatic sulfonic acids.

The M_w became the highest and with MSA whose $T_{d,5\%}$ was as low as 80 °C and the second highest with DBSA whose $T_{d,5\%}$ temperature was over 220 °C. With the other sulfonic acids whose $T_{d,5\%}$ was equal to or higher than the SSP temperature (150 °C), the M_w increase was rather limited because they gradually degraded with the progress of SSP. The M_w increase must be determined by how much residual catalyst was present in the polymer. The most interesting was that MSA showing a $T_{d,5\%}$ much lower than the SSP temperature gave the highest M_w, which will be discussed in the later section. In contrast, the molecular weight retention of PLLA after the melting process showed an opposite relation. Namely, the M_w retention became remarkably higher with p-XSA and p-TSA with $T_{d,5\%}$ ranging from 150–180 °C than with MSA and DBSA. Probably, the sulfonic acid catalysts could be removed by thermal decomposition when $T_{d,5\%}$ was lower than T_m of PLLA, while they survived to promote the degradation of PLLA in case $T_{d,5\%}$ was higher than T_m of PLLA.

In order to detect the sulfonic acid catalysts remaining in the polymer, the PLLA products obtained after the SSP were extracted with acetone, and the acetone extract was analyzed by ^{1}H NMR spectroscopy. Fig. 3.4 shows the ^{1}H NMR spectra of the acetone extracts from the polymers prepared with DBSA (A), MSA (B), and p-XSA (C). The extract from the polymer prepared with DBSA clearly showed signals of DBSA in addition to those of PLLA oligomer, supporting the involvement of DBSA in the SSP product. On the other hand, the extract from the polymer prepared with MSA showed no signal of MSA, indicating little residual catalyst in the SSP product.

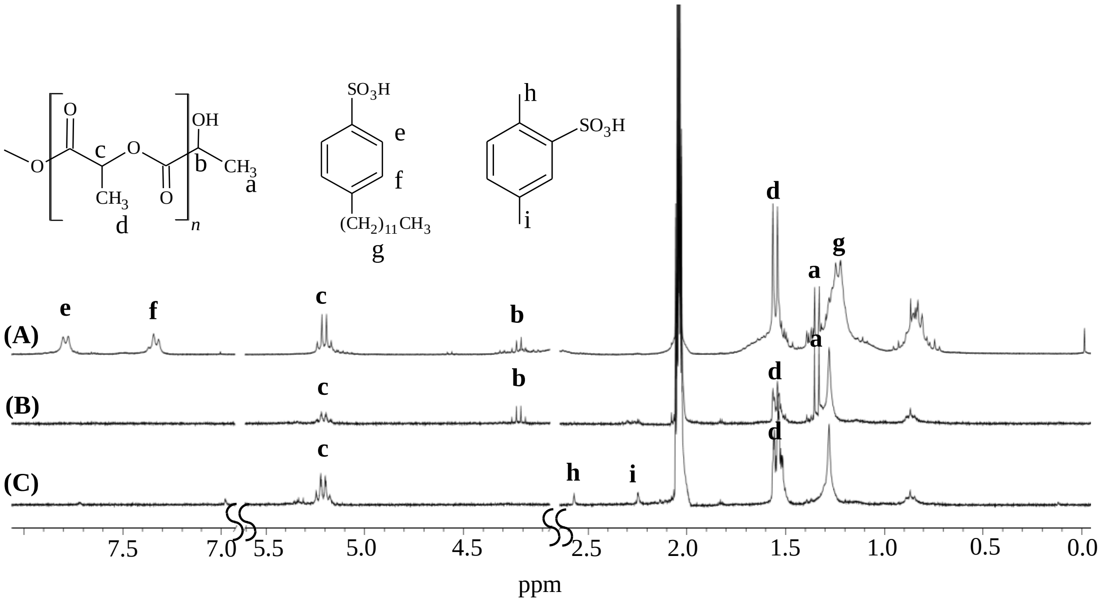


Fig. 3.4. ^{1}H NMR spectra of the acetone extracts from the PLLA products prepared by SSP at 150 °C for 15 h; with (A): DBSA, (B): MSA and (C): p-XSA as the catalysts

The extract from the polymer prepared with p-XSA showed very small signals of p-XSA. The amounts of extracted products were 4% with DBSA and less than 0.5% with p-XSA. The extracts comprised mainly of PLLA oligomers and catalysts. Since the $T_{d,5\%}$ of DBSA (228 °C) was much higher than the SSP temperature, it could survive the melting process at 220 °C and caused the remarkable M_w decrease by the thermal degradation involving hydrolysis by a trace amount of moisture, zipper-like depolymerization, random oxidative main-chain scission, and inter- and intramolecular transesterifications to monomer and oligomers [19]. When the SSP sample was washed with acetone to remove the residual DBSA, it was found to retain high molecular weight even after the melting process. This fact indicated that the remaining sulfonic acid catalysts should strongly affect the thermal stability of the PLLA polymer.

Different from the PLLA prepared with DBSA as the catalyst, the PLLA prepared with MSA did not involve any residual catalyst because the ^{1}H NMR spectrum of its acetone extract (Fig. 3.4 B) showed no signal due to MSA. It was however found out that the sulfur content in the PLLA polymer obtained with MSA as the catalyst reached almost 400 ppm. This fact suggested that some sulfur substance was involved in the polymer to play catalytic activity. As depicted in Fig. 3.1, the thermal decomposition behavior of MSA indicated a significant weight loss above 92 °C below which moisture had been removed. Since MSA has three electron-donating methyl groups, it is unstable and readily involved in desulfonation. The liberated SO_3 ought to migrate into the reactant to produce a sulfonated lactic acid or exist in the form of sulfuric acid even after SSP. These sulfonated products or sulfuric acid can catalyze not only SSP but also thermal degradation of PLLA in the melting process to remarkably decrease the molecular weight. In fact, it has been reported that sulfuric acid can give a high-molecular-weight PLLA in the direct polycondensation of PLLA despite causing discoloration [13]. In addition, these sulfonated products or sulfuric acid formed in situ should also promote hydrolysis and transesterification of PLLA to lead the M_w decrease and discoloration in the melting process. Since the acetone-washed PLLA sample, which had been polymerized with MSA catalyst, showed a high molecular weight retention after the melting treatment, the sulfonated products or sulfuric acid could be removed from the polymer by washing. If such an acetone washing is allowed in the industrial production, MSA can be an effective catalyst for obtaining high-molecular-weight PLLA.

Interestingly, the PLLA obtained with p-XSA as the catalyst exhibited high thermal stability, i.e., low M_w decrease was observed in the melting process at 220 °C, because only a small amount of residual catalyst was detected in the polymer. However, p-XSA was somewhat inferior to MSA and DBSA in terms of increase in M_w of PLLA after the SSP. Since the decomposition of p-XSA began above 130 °C, p-XSA was slowly decomposed during the SSP to give a limited M_w increase of PLLA.

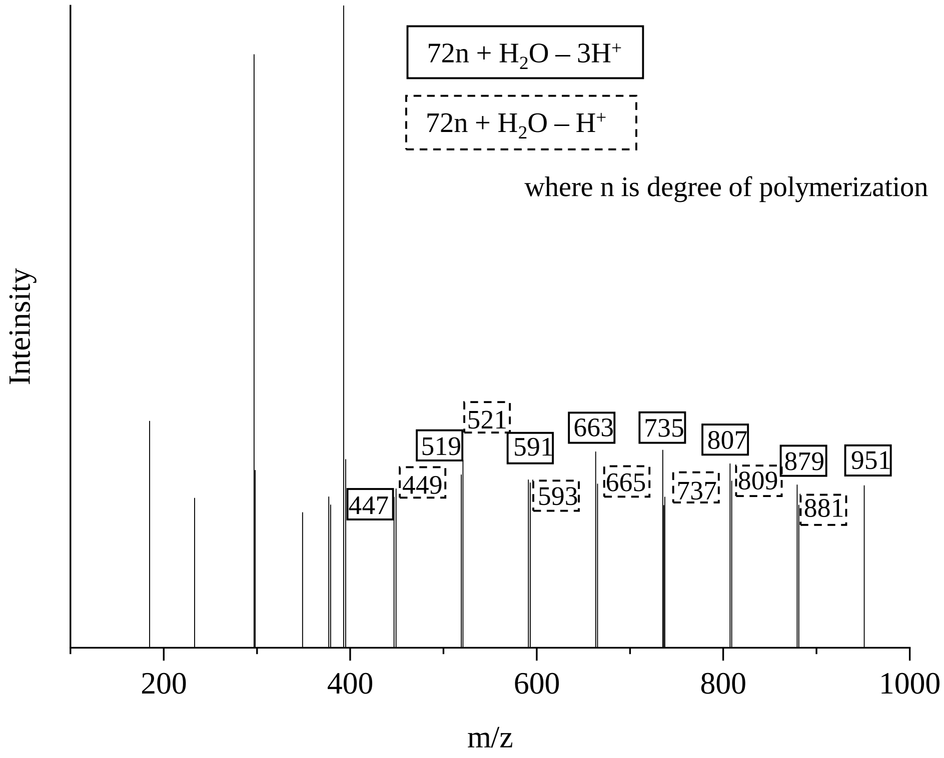
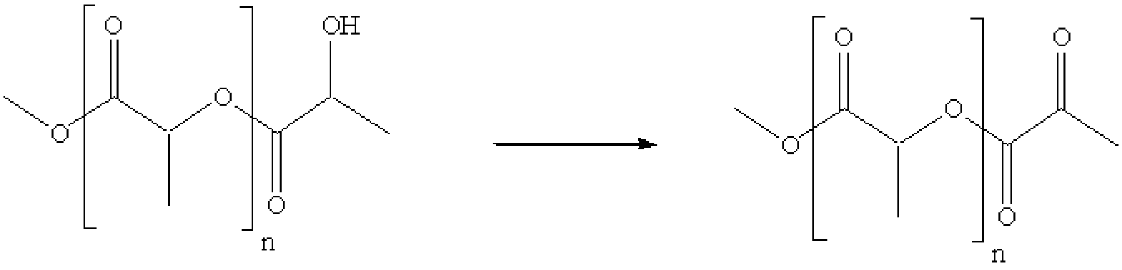


Fig. 3.5. A typical MS spectrum in the negative mode of the acetone extract from the PLLA prepared with p-XSA as the catalyst.

Fig. 3.5 shows a representative MS spectrum of an acetone extract of a PLLA polymer obtained by the SSP with p-XSA as the catalyst at 150 °C. Two sets of mass peaks were detected with an increment of 72 in mass number, which corresponds to the molar mass of a lactate unit. The difference in molar mass between each set of the mass peaks was two. The peaks of higher mass numbers were reasonably attributed to molecular ions of lactic acid oligomers having both hydroxyl and carboxylate ion terminals (72n + H_2O – H^+ where n is degree of polymerization). The peaks of lower mass numbers were reasonably assigned to the lactic acid oligomers having a different terminal group, which ought to be carbonyl group instead of hydroxyl group. The formation of this carbonyl terminal may be attributed to the thermal oxidation shown in Scheme 3.2.



Scheme 3.2. Proposed mechanism of oxidation of lactic acid terminal of PLLA

The ^1H NMR spectrum (Fig. 3.4(C)) of the same acetone extract from the PLLA obtained with p-XSA as the catalyst exhibited no signal at δ 4.3 ppm due to the terminal hydroxy-methine protons, supporting the formation of cyclic oligomers. However, the carbonyl-methyl signal was absent, because of the least amount of such oligomers with a carbonyl terminal. They may have therefore been formed from the oligomers during the MS measurement. More detailed investigation is needed concerning the discoloration and side reactions.

3.4.4. Optimum Conditions for the Solid-state Polycondensation Processes

The above data suggested that when the reaction temperature of SSP is lowered the degradation of sulfonic acid catalysts can be retarded, for better control of the SSP processes. In order to obtain a PLLA having high molecular weight and high thermal stability, the reaction conditions of the whole SSP processes covering from the annealing for crystallization of the PLLA prepolymer (oligomeric melt-polycondensate of L-lactic acid) to the thermal treatment for catalyst removal (for decomposing the sulfonic acids) were optimized. The approach of this study to this optimization was to precisely control the temperature of each elementary process based on the $T_{d,5\%}$ of the sulfonic acid catalyst and the T_c and T_m of PLLA. Fig. 3.6 shows the temperature scale involving the respective elementary processes by using p-XSA as the catalyst whose $T_{d,5\%}$ is resided in the most convenient temperature range for the process control.

Since the $T_{d,5\%}$ of p-XSA is 155 °C, the SSP temperature should be significantly lower than this temperature.

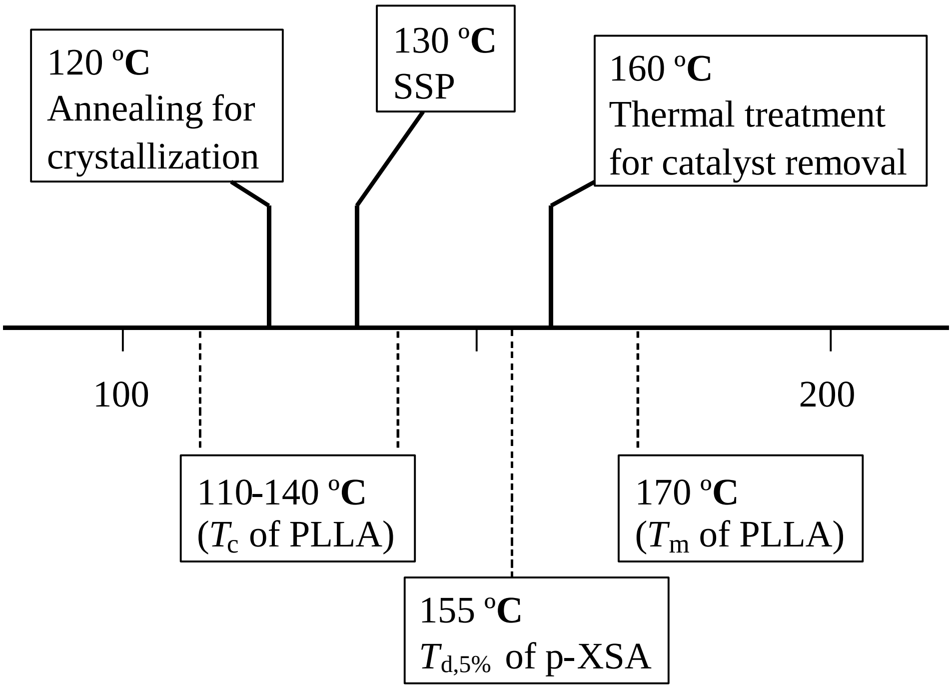


Fig. 3.6. An optimum temperature profile for the whole SSP processes to obtain high-molecular-weight PLLA having high thermal stability.

In the SSP described above, the SSP temperature was set at 140–150 °C, and its thermal decomposition was slowly induced during the long reaction time to give a slightly lower M_w of the PLLA finally obtained. Therefore, the SSP temperature must be set at 130 °C at which the gradual decomposition of p-XSA ought to be prevented during the SSP. On the other hand, the thermal treatment for catalyst removal must be done at temperature which is above $T_{d,5\%}$ of p-XSA and below T_m of PLLA to maintain solid (or crystalline) state of the PLLA product. Here, it can be done at 160 °C in spite of a narrow temperature window available. As for the annealing for crystallization of the PLLA prepolymer, the temperature must not be so high as to cause melting of the PLLA precursor within the temperature range of T_c. It can be set at 120 °C as described in the previous SSP processes. The SSP temperature is also preferably in this T_c range to enhance quick crystallization of the chain-extended PLLA molecules.

With the above reaction conditions in mind, the SSP was re-examined. The results are shown in Table 3.4. Although the M_w of the finally obtained PLLA was not enough high when the SSP was conducted at 130 °C for 15 h with a catalyst amount of 0.25 mol%. It was however found out that M_w of the PLLA reached 160,000 Da after the same SSP by increasing the catalyst amount to 0.5 mol%. The PLLA product obtained was whiter in appearance than that obtained by the above SSP conducted at 150 °C. This result revealed that the M_w of PLLA can be higher with little side reaction occurring even though significantly larger amount of catalyst was added. The removal of the p-XSA catalyst was successfully performed by the thermal treatment of the resultant PLLA polymer at 160 °C for 5 h.

Table 3.4. Results of the SSP processes with optimum conditions by using p-XSA as the catalyst.

p-XSA catalyst (mol %)	SSP					Catalyst removal	Melting at 220 °C		
	M_w $(10^4)^a$ 120 °C-5 h	M_n $(10^4)^a$ 120 °C-5 h	M_w $(10^4)^b$ 130 °C-15 h	M_n $(10^4)^b$ 130 °C-15 h	Color	M_w $(10^4)^c$ 160 °C-5 h	M_w $(10^4)^d$ 220 °C-0.5 h	M_n $(10^4)^d$ 220 °C-0.5 h	M_w retention^e (%)
0.25	0.9	0.3	10.2	4.9	white	12.6	11.1	6.0	88
0.5	2.9	0.8	16.0	6.8	white	17.9	15.0	6.7	84

[a] SSP at 120 °C under 10 Torr for 5 h.

[b] SSP at 130 °C under 10 Torr for 15 h.

[c] M_w of PLLA after thermal treatment at 160 °C under 10 Torr for 5 h.

[d] PLLA after melting test at 220 °C for 0.5 h.

[e] M_w of PLLA after melting relative to the initial M_w of PLLA in %.

In this case, the M_w of PLLA even increased to 179,000 Da. Fig. 3.7 compares the TGA profiles of the PLLA polymers obtained before and after the thermal annealing as well as with the profile of a commercially available PLLA sample (control) that was synthesized by the ROP method.

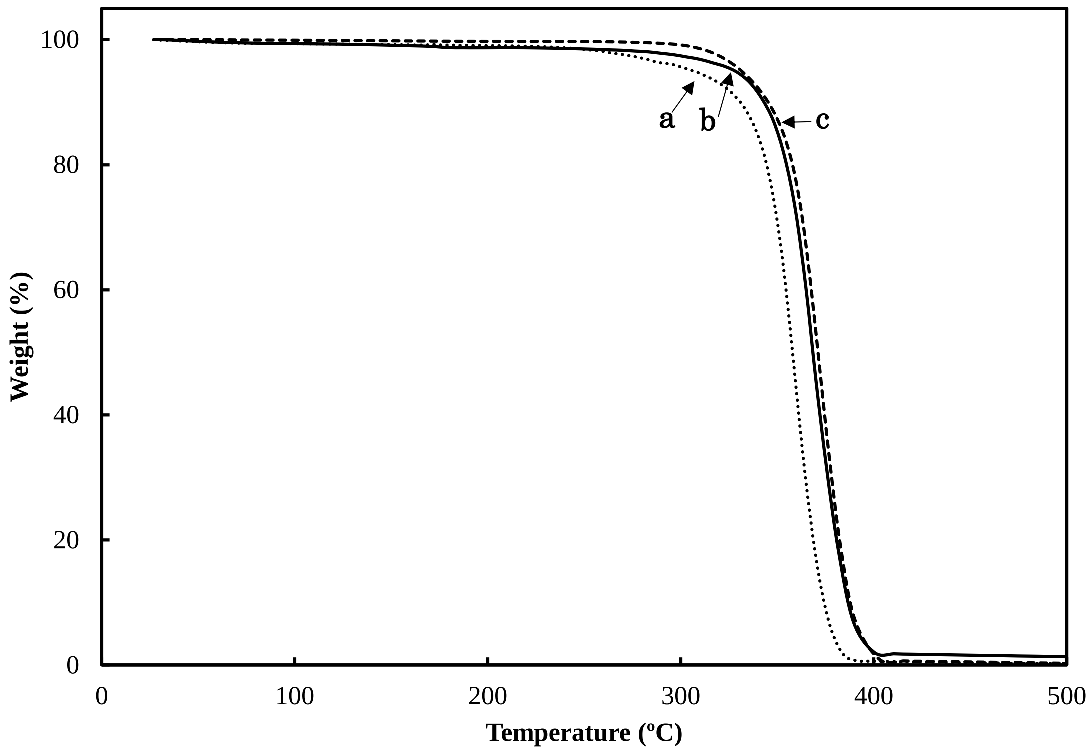


Fig. 3.7. TGA profiles of PLLA prepared by SSP with p-XSA; at (a) 130 °C for 15h, (b) 160 °C for 5h and (c) a commercial PLLA sample (LAYCIA®: control).

It was indicated that the $T_{d,5\%}$ of the PLLA increased from 306 to 337 °C after the thermal treatment, which almost corresponded with that of the control sample. After the melting test at 220 °C, the M_w of this PLLA decreased to 150,000 Da, showing a M_w retention as high as 84%. Comparison of the present PLLA product with the commercial PLLA products (U’z® S-06 and LAYCIA®) that were synthesized by the lactide method, no difference in quality was noted. In the current process, the catalyst loading is ten times higher than that in the tin-catalyzed ROP of lactide used for the commercial PLLA production. Even in such a high catalyst loading, it is readily removed from the products, and the decomposition products from the catalysts can be effectively captured by active charcoal and other devices, giving little environmental pollution. It was therefore concluded that the present direct polycondensation method using an aromatic sulfonic acid having a $T_{d,5\%}$ value of about 150 °C as the catalyst is really practical to obtain a PLLA having high molecular weight and high thermal stability.

3.5. Conclusion

In this study, the melt/solid-state polycondensation of PLLA catalyzed by aromatic sulfonic acids was investigated in detail to determine the optimum reaction conditions to obtain a high-molecular-weight PLLA having high thermal stability. It was found out that the structure of sulfonic acid catalysts strongly affects the M_w and thermal stability of the finally obtained PLLA. It was because the thermal decomposition temperature (desulfonation) of the aromatic sulfonic acids was different depending on the type and number of substituents. We found that m-XSA, p-XSA, and p-TSA, showing a $T_{d,5\%}$ around 150 °C that is lower than T_m of PLLA, can be the best catalyst for the SSP. With MSA whose $T_{d,5\%}$ is lower than 100 °C, sulfuric acid generated by desulfonation was thought to promote the SSP although it also enhanced the thermal degradation of PLLA. In contrast, with a more stable DBSA whose $T_{d,5\%}$ is higher than 200 °C, it remained in the PLLA product to cause M_w decrease by the enhanced thermal decomposition. The oligomeric fractions of the PLLA products were extracted with acetone and analyzed by ^{1}H NMR and MS spectra. It was confirmed that the aromatic sulfonic acids received decomposition during the SSP for long time. Therefore, the optimum process temperatures were determined in reference to the $T_{d,5\%}$ of the aromatic sulfonic acids as well as the T_c and T_m of PLLA. By this way, the catalyst decomposition during the SSP was efficiently suppressed, and catalyst removal from the SSP products was efficiently performed to obtain the PLLA with high molecular weight and high thermal stability. This method is considered to be an effective direct polycondensation method that can replace the lactide method.

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Chapter 4

General Conclusion

The purpose of this study is to advance the direct polycondensation method of LLA, which is expected to lower the cost of polymerization process from the current ROP. For this purpose, this thesis focused on the elucidation of the factors influencing the molecular weight and thermal stability of PLLA in direct polycondensation. This thesis consists of four chapters, the essence of each chapter is as follows.

In Chapter 1, it was reported on background of this thesis and present state regarding the production of PLLA. Especially the present state and problems in the direct polycondensation of PLLA were summarized and the purpose of this study was described.

In Chapter 2, Relationship between the increase in molecular weight and evolution of crystal structure was studied in the SSP of PLLA. Here, a PLLA prepolymer having a M_w of c.a., 3000 Da and a high *OP* over 99 %ee was prepared by bulk melt-polycondensation of LLA with DBSA as a catalyst.

It was first annealed at 80–110 °C and subjected to SSP at 120–140 °C to obtain a PLLA polymer having an M_w higher than 100,000 Da. The highest increase in M_w was observed at 140 °C, while the growth of crystal structure had been induced in an early stage of SSP at 120 °C, reaching 71% in crystallinity. Wide- and small-angle X-ray scatterings of the PLLA polymers revealed that the PLLA polymer retained the α-form crystals throughout the annealing and SSP with little change in lamellar morphology. It was therefore suggested that the acid-catalyzed polycondensation is driven by the reaction of the terminal groups of the PLLA prepolymer accumulated on the surface ab planes of the lamellar crystals above 120 °C. Therefore, the crystal morphology of the annealed samples was found to strongly influence the final molecular weight of PLLA in the SSP.

In Chapter 3, MP/SSP of PLLA was conducted by using several aromatic sulfonic acids as the catalysts. It was clarified that the increase in molecular weight and the thermal stability of the obtained polymer are correlated with $T_{d,5\%}$ of the sulfonic acids determined by thermal gravimetric analysis. When 2,5-dimethyl-, 2,4-dimethyl- and 4-methyl-benzenesulfonic acids showing $T_{d,5\%}$ around 150 °C were used as the catalysts, PLLA polymers with high molecular weight and excellent thermal stability could be obtained. On the other hand, 2,4,6-trimethylbenzenesulfonic acid showing $T_{d,5\%}$ around 100 °C and 4-dodecylbenzenesulfonic acid with $T_{d,5\%}$ above 200 °C gave PLLA polymers with remarkably low thermal stability. The residual catalyst involved in the product polymer or SO_3 generated during the polymerization decreased the thermal stability of the polymer. The oligomeric fractions of the PLLA products were extracted with acetone and analyzed by ^{1}H NMR and mass spectra. It was verified that the catalyst had efficiently been removed by thermal annealing while it remained active during the SSP to produce a thermally stable PLLA with high molecular weight.

In Chapter 4, as described above, it was found that the crystal morphology of the annealed samples strongly influenced the final molecular weight of PLLA in the SSP. The crystalline morphology of the annealed sample is an important factor in the SSP and a well-oriented state of the helical chains of the PLLA prepolymer must be realized in the crystallization step for obtaining a high-molecular-weight PLLA. Furthermore, the investigation relating to the thermal stability of PLLA by catalyst revealed that the increase in molecular weight and thermal stability of PLLA was related to $T_{\mathrm{d},5\%}$ of sulfonic acid. By this findings, it was found that a process to efficiently suppress catalytic decomposition in SSP and efficiently remove catalyst from SSP product. The process obtained PLLA with high molecular weight and high thermal stability.

These achievements of this study are considered to be superior in promoting direct polycondensation of PLLA toward industrialization. In the future, it is expected to further increase the molecular weight of the PLLA by controlling the molecular orientation of the PLLA prepolymer. Moreover, it is expected that the promotion of direct polycondensation into industrialization will be promoted by the scale-up study using the 2,5-dimethyl-, 2,4-dimethyl- and 4-methyl-benzenesulfonic acids as the catalyst found in this study.

Publication List

1. **Molecular weight increase driven by evolution of crystal structure in the process of solid-state polycondensation of poly(L-lactic acid)**, Makoto Takenaka, Yoshiharu Kimura, Hitomi Ohara, Polymer 126 (2017) 133–140 doi.org/10.1016/j.polymer.2017.08.036

2. **Influence of decomposition temperature of aromatic sulfonic acid catalysts on the molecular weight and thermal stability of poly(L-lactic acid) prepared by melt/solid state polycondensation**, Makoto Takenaka, Yoshiharu Kimura, Hitomi Ohara, Polymer 155 (2018) 218–224 doi.org/10.1016/j.polymer.2018.09.046

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